Physicochemical Studies of the Organic Dyestuffs in Relation to Photochemistry. I. Effect of Light on the Adsorption Equilibrium

By Masao KOIZUMI and Masashi IMAMURA

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Introduction

Organic Dyestuffs are a very interesting group of substances from the photochemical standpoint. Of late, structures of some dyestuffs were discussed quantum-mechanically, and the theory of color hasmade much progress. However, photochemical studies are rather few; it is true that there are various kinds of investigations on the chlorophyll, which is important in assimilation, and on the photographic sensitizers, but it is desirable to investigate photochemically various other organic dyestuffs from a more general standpoint. Especially it seems necessary to study the behavior of dyestuffs in the colloidal system or the interaction between high-polymers and the dye molecules, since the dyes often play an important role in biological systems which can be considered as such complex systems.

With these ideas in mind, we have begun to study the photochemical behavior of dyestuffs, and at first have chosen the problem whether the adsorption equilibrium of dyestuff is affected by the illumination or not, when it is adsorbed on the colloidal surface from aqueous solution.

Investigations of this kind were already done by Hedvall[1], who found that when some dyestuffs are adsorbed, for example, on HgS or on ZnS from aqueous solution, illumination causes a remarkable change in the quantity of adsorption. His interest, however, was confined chiefly to the change of electronic structure of adsorbent produced by illumination. Our interest, on the contrary, is concerned with the problem whether the adsorption equilibrium is influenced by the participation of the excited dye molecules produced by illumination. As the adsorbent, therefore, the transparent substances such as silica gel or alumina were chosen. At the beginning, let us consider briefly whether there can be such possibility or not. The following two cases may be important for it.

Possibility (1). If the life of an excited molecule (or the metastable state, as the case may be) produced by illumination is much longer than the mean time of duration of the adsorbed state of a dye molecule, we may conceive two adsorption equilibria, one for the ground state and the other for the excited state. Then the adsorption potential will, in general, be different for these two states, and we can anticipate the effect of illumination in this case.

Possibility (2). This case is concerned with the dissipation of light energy absorbed by the dye molecule in the adsorbed state, and is rather independent of the life of the excited molecule. In general, the excess energy which the molecule gains by the absorption of photon dissipates as thermal energy, except when photochemical change or luminescence takes place. If the dissipation of energy happens to take place selectively toward the adsorbent-side rather than the solvent-side, the temperature of the adsorbent surface may rise locally, which will cause the decrease of the quantity of adsorption. This circumstance may, perhaps, be considered as the selective transfer of the excess energy into the bond of adsorption[2].

The First Experiment and its Results

The adsorption experiment was done in the evacuated state, with silica gel or alumina preliminary evacuated at a moderate temperature and the aqueous solution of dye also evacuated previously. In order to examine the light effect, we prepared two similar adsorption systems at one time and attached them on the disk, which was rotated in the thermostat, one system under illumination and the other in the dark, for eight hours, and

(1) Hedvall, *Z. Physik. Chem.*, **B32**, 383 (1936) etc.

(2) That such a possibility does really exist may be inferred, for example, from the fact that CO attached to the hemoglobin molecule is detached by illumination nearly quantitatively. (Cf. O. Warburg, "Naturforschung u. Medizin in Deutschland", 1939-46, Band 39, Biochemie Teil I.)

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then compared the quantities of adsorption in the two systems. For this comparison, we measured with Pulfrich photometer the concentration of the dye in the solution, which was separated from silica gel after the experiment.

Dyestuffs used in this experiment were Rhodamine 6G, Rhodamine B, Flavophosphine, Trypaflavin, Acridine orange, Methylene blue, Pinacyanol iodide (all of them were adsorbed on silica gel), Erythrosine, and Uranine (for the last two, the adsorbent was alumina). For the illumination, we placed three 100 watt tungsten lamps, 20 cm. in length, parallel and 10 cm. apart from the reaction vessel. The number of photons which arrived at the reaction vessel was about $10^{15}/cm^2 \cdot sec$. The experimental results were such that we could perceive the light effect in only one case, which was Rhodamine 6G adsorbed on silica gel. Some dyes were discolored by the illumination and none of the others showed any light effect beyond the experimental error.

Some of the results for Rhodamine 6G are tabulated in Table 1.

Table 1

Temp.: 20°C.

Initial conc. (μM/l.)	Dark		Light	
	Equilibrium conc. (μM/l.)	Adsorbed quantity (μM/g.)	Equilibrium conc. (μM/l.)	Adsorbed quantity (μM/g.)
10	1.2±0.2	0.066	1.6±0.2	0.063
	1.2±0.2	0.066	2.1±0.2	0.054
50	2.9±0.2	0.354	3.1±0.2	0.352
	2.9±0.2	0.354	3.1±0.2	0.352
100	4.0±0.2	0.720	4.8±0.2	0.710
	3.4±0.2	0.725	5.5±0.2	0.715
200	7.4±0.5	1.445	9.2±0.5	1.430
	6.3±0.5	1.452	7.4±0.5	1.445
400	15.4±0.5	2.895	20.8±0.5	2.844
	16.5±0.5	2.880	19.8±0.5	2.852
600	48.2±2	4.14	48.2±2	4.14
	49.5±2	4.13	47.7±2	4.15
800	135 ±5	4.99	138 ±5	4.97
	122 ±5	5.09	138 ±5	4.97
1000	243 ±5	5.67	240 ±5	5.70
	249 ±5	5.63	180 ±5	6.14

In Table, 1, initial conc. means the concentration of dye solution before the experiment, Equilibrium conc. is the one after the adsorption experiment. The adsorbed quantity was calculated from the above two quantities. The adsorption isotherms in the dark and the light are shown in Fig. 1. from which one can find the quantity of decrease in the adsorbed dyestuff caused by the illumination.

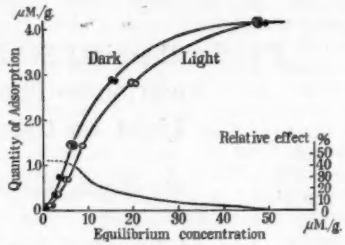

Fig. 1.—Adsorption isotherms in dark and light and the relative effect, for Rhodamine 6G.

The Second Experiment and its Results

In this experiment we used the vessel as shown in Fig. 2, in order to compare the quantity of adsorption in light and dark for the same one sample. This vessel also enabled us to study the effects of various factors for the same sample, such as light intensity, temperature, or the wave-length of light. The apparatus and the experimental procedure were as follows. The evacuated silica gel and the dye solution were placed in A. After the vessel was sealed off at B, it was shaken moderately in the thermostat and brought to the adsorption equilibrium in the specified condition, for example, light and dark, or at a certain light strength and at a certain temperature. The part A was illuminated by 100 watt tungsten lamp placed in the metal case which was attached close to this part. Glass filters were inserted between A and the light-source to test the effect of the wave-length of light. The intensity of light was varied by adjusting the voltage. The relation between voltage and light intensity through the filter (Matsuda V-G1) proved to be almost linear in the range from 20 to 90 V. With the same filter and at 20 V., the number of photons which were absorbed by the dye molecules in the vessel were about $10^{15}/cm^2 \, sec$.

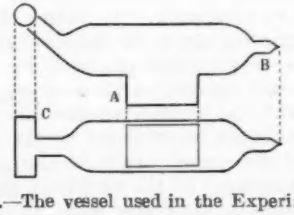

Fig. 2.—The vessel used in the Experiment II.

The determination of the dye concentration of the solution was done as follows. The solution was poured into B which acted as a

cell part for the photometric measurement. With the photomultiplier and galvanometer, the dye concentration was determined with an accuracy of about 0.05 μM/l. in favorable conditions. When one measurement was finished, part of the adsorbed dye was desorbed by warming the vessel at 40°C. for twenty to forty minutes and thus prepared for the next experiment. With such an apparatus and procedure, we performed the experiment over and over again using the same sample in different conditions.

Some of the results are tabulated in Table 2.

Table 2

Rhodamine 6G, initial concentration: 100 μM/l.

	Dark	Light		
Temperature °C.	Equilibrium concentration (μM/l.)	Equilibrium concentration (μM/l.)	Filter (Matsuda color filter)	Voltage (Volt)
25	2.4	2.55	V—G1	40
	2.35	2.6	V—G1	90
	2.4	2.6	V—G1	20
	2.4	2.35	V—R3	50
20	1.95	2.1	V—G1	90
	2.0	2.1	V—G1	50
	2.0	2.1	V—G1	20
	2.0	2.1	V—G1	15
15	1.5	1.65	V—G1	70
	1.6	1.7	V—G1	60
	1.5	1.75	V—G1	60
	1.6	1.75	V—G1	60
	—	1.8	V—G1	20
		1.8	V—G1	20
10	1.55	1.75	V—G1	60
	1.5	1.7	V—G1	60
	1.5	1.7	V—G1	60
	1.5	1.55	V—R3	50
	—	1.6	V—R3	50

From this Table it is apparent that

(1) the illumination increases the equilibrium concentration which is to be attributed to the decrease in the quantity of adsorption, although it is considerably small as compared with the results of experiment I,

(2) when the voltage of the light source is reduced below 20 V., no light effect is perceived; but in the range from 20 to 90 V., an almost constant effect, 0.2 μM/l. in equilibrium concentration is observed,

(3) the light which is not adsorbed by Rhodamine 6G cannot cause any effect, and

(4) temperature effect lies within the experimental error.

Discussion

From the above results we can definitely say that, when Rhodamine 6G is adsorbed from the aqueous solution onto silica gel, the illumination causes a decrease in adsorbability.

As for the mechanism of this phenomenon, the second possibility mentioned in "Introduction" is more favorable than the first one. Though various facts obtained by the experiment can be explained from this view point, here, we will only mention the following discussion which denies the first possibility definitely.

(1) If the first possibility is applied to this phenomenon, the number of excited molecules (or the metastable molecules) existing in the steady state must, at least, exceed the quantity of decrease in adsorption. The relation between the number of photons, q, which are absorbed per sec. (per cm^2. of the illuminated area), and the number of excited molecules, N_0, which exist in the steady state (per cm.^{2} of the illuminated area), should be represented by the equation

$$q = 1/\tau \cdot N_0,$$

where τ is the mean life time of the excited molecules. As the number of photons absorbed per cm.^{2} is 10^{15} at 20 V. of the light source,

$$N_0 = 10^{15}\tau \qquad (1)$$

Now the difference of equilibrium concentration of dye is 0.2 μM/l. for 2 g. silica gel, the volume of the solution is 30 cc. and the illuminated area is about 15 cm.^{2} Therefore, the number of decrease in adsorbed molecules for a unit area of the illuminated surface is

$$\Delta N = 0.2\times10^{-6}\times30/1000\times6\times10^{23} \times 1/15 \approx 2\times10^{15} \qquad (2)$$

Even with an assumption that the excited molecule does not adsorb at all, the condition $N_0 = \Delta N$ demands that τ should be of the order of 1 sec. The life time of the excited molecule of the fluorescent dyestuff is in general of the order of 10^{-8} sec. or less, and, in addition, there is no evidence of any metastable molecule in the solution of Rhodamine 6G, so that we may definitely conclude that the first possibility can not be realized in the case of Rhodamine 6G.

(2) If the effect is due to the second possibility, the adsorbed dye molecules which absorb photons are to desorb more easily than the ordinary ones, and the magnitude of the

effect depends upon the difference between the rate of adsorption and desorption in the illuminated system, and so we can expect an effect of some magnitude, large or small, according to the circumstances. Thus the experimental results that the decrease in the number of adsorbed molecules as large as 2×10^{15} is produced by relatively small number of photons, 10^{15} in the order, does not contradict the second possibility. But a difficulty which must be explained when we adapt the second possibility is the phenomenon of photosaturation that is reached already with absorption of ca. 10^{15} photons or more per cm.^{2} per sec. In the second mechanism, such a photosaturation cannot simply be explained as shown by the following estimation. In the steady state, the following relation (3) must hold between the number of molecules desorbed in excess by illumination and the excess number of molecules which attack the adsorbent surface; the former will be given as κq, where q is the number of photons absorbed per sec. and κ the probability factor of desorption due to illumination, while the latter may be put as a Δn, where Δn is the excess number of dye molecules produced by illumination in the neighborhood of adsorbent, and a is the specific rate of adsorption of the dye molecule.

$$\kappa q = a\cdot\Delta n \qquad (3)$$

According to the equation (3), Δn, and hence the decrease of adsorption must increase proportionally to the increment of q. From the experimental results the number of adsorbed dye molecules per cm.^{2} of the illuminated area is 10^{17}, which is much larger than 10^{15}, the number of photons absorbed per cm^2. at 20V., and so we can not expect the photo-saturation with the light intensity of this order if all of the adsorbed dye molecules can take part in present photo-effect. In connection with this difficulty, however, it may not be useless to note the following speculation.

In the aqueous solution of Rhodamine 6G, some of the dye molecules exist in the dimerized state. When the dye is adsorbed on the high-polymer, for example polyvinylalcohol sulfonate[3], the dimer molecule adsorbs 100 times more than the monomer. If we assume that, as is very plausible, the similar situation exists in the present system, and that only the monomer adsorbed on the surface participates in the photo-effect, then the above situation might be expected when the number of monomer happens to be far less than that of photons absorbed. This speculation may be rather probable, because the monomer has a strong power of fluorescence while the dimer has none, and thus there is no doubt that the mechanism of the energy dissipation is much different for both molecular species.

We want to add some notes on the results of the first experiment. First: there exists some difference in the magnitude of the effect in experiment I and II; it can probably be attributed to the difference in experimental conditions. Second: the light effect in experiment I varies with the concentration of the solution as is shown in Fig. 1; this can be explained as due to the shielding action of the solution if we take the following two circumstances into account. In the first place, the light intensity in the first experiment is of the order that the photo-saturation commences in the second experiment. In the second place, the condition in the experiment I is such that the light must pass through a layer of solution of a moderate thickness before it reaches the adsorption surface. Thus the intensity of light which passes through the solution and arrives at the adsorbent is reduced according to Beer's law. From this point of view, we could in fact explain the results of Fig. 2 almost quantitatively.

Details of the experiments and full discussion will be published in the Journ. Inst. Polytechnics, Osaka City University. The authors would like to express their gratitude to Mr. S. Kato and Miss A. Watanabe for much help in experiments. The present investigation was supported in part by a grant from the Ministry of Education.

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(3) M. Koizumi and N. Mataga, to be published in the near future.

Physicochemical Studies of Organic Dyestuffs in Relation to Photochemistry. II. Influence of the Addition of K-Polyvinylsulfate upon the Absorption Spectra and Fluorescence of Rhodamine 6G in Aqueous Solution

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Introduction

We have taken up the investigation of metachromasy, as the first step towards the study of the interaction between high polymers and organic dyes.

There are some experimental works reported on this phenomenon,[1][2][3] but the general theory which is applicable to all cases has not yet been established; the phenomenon seems in general to be very complicated and perhaps may not be explained from a single view-point. Among various ideas proposed for the mechanism, the following two seem to be most noteworthy.

(1) According to the first idea, metachromasy is considered as a result of some change in the electronic structure of dye ion which is caused by the electrostatic interaction between high-molecular-weight electrolyte and dye ion.[3]

(2) According to the second idea, it is attributed to the change of aggregation of dye ions which results from the adsorption of the latter upon high polymers.[1][2]

These two ideas do not, as we believe, contradict each other. There may exist some cases which can be comprehended simply by the first theory and others which can be explained only by the second theory. In general, however, there will be many cases which can be interpreted correctly only when both of the two theories are taken into account.

In the following discussion the above two cases will be called the ideal case (1) and case (2), respectively. For the systematic investigation of metachromasy, it is desirable, we believe, to search at first for such ideal cases which can be fully explained as case (1) or case (2). For this search, the following arguments might be of some help. If the metachromatic molecule has only one functional group and is of relatively low molecular weight, and the aqueous dye solution obeys Beer's law, then such a system may have a greater chance to be treated as the case (1). On the other hand, the case (2) may be found in those systems where the metachromatic molecule has more than two functional groups of weak nature, and the dye does not obey Beer's law.

Now the aqueous solution of Rhodamine 6G shows, on one hand, only feeble metachromasy by the addition of K-Poly-vinylsulfate (P. V. S. K.),[3] which is rather a strong metachromatic substance, while, on the other hand, some of the Rhodamine ions are in the dimerised state in the aqueous solution, the fraction of the dimer increasing with the concentration according to the mass action law.[4] On the ground of these facts already reported by other investigators, we considered that Rhodamine 6G-PVSK system might be treated as the case (2), and it has been confirmed to be the case by the present systematic study over a wide range of concentrations both of the dye and PVSK.

The purpose of this paper is to show how the change in the absorption spectra of the Rhodamine 6G aqueous solution caused by the addition of PVSK can be interpreted quantitatively as the ideal case (2). In addition we will report some experimental results on the quenching of fluorescence of Rhodamine 6G by PVSK, and will discuss them on the same ground.

Experimental

For the measurement of absorption spectra and the relative intensity of fluorescence, Beckman Spectrophotometer Model D. U. was used.

PVSK was obtained by the sulfonation of polyvinyl alcohol of which the polymerization

(1) L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **67**, 1212 (1945).
(2) L. Michaelis, *J. Phys. & Colloid Chem.*, **54**, 1 (1950).
(3) Terayama, *Kagakuno Ryoiki*, **1**, 71 (1947).
(4) W. L. Levshin, *Acta Physicochim. U. R. S. S.*, **1**, 681 (1935).

degree was 1800. Two samples were prepared whose degrees of sulfonation were determined to be 61 % and 36 %.

The experimental results can be summarised as follows.

(a) The absorption spectrum of Rhodamine 6 G in aqueous solution has a peak at 526 $m\mu$ with a small shoulder at 500 $m\mu$ when dilute, while as the concentration increases, the latter grows gradually, the former reducing at the same time. This observation is the same as reported by other investigators and the peaks at 526 $m\mu$ and at 500 $m\mu$ are considered respectively to be due to the monomer (M-Band) and the dimer (D-Band).[4]

(b) The molar fluorescence intensity, F/C (where F is the intensity and C is the analytical concentration of dye in mol. mol./l.) remains constant from very dilute solution up to 5×10^{-6} mol/l., but beyond this value, it decreases monotonously with increasing concentration and approaches zero asymptotically.

(c) When PVSK is added step by step to the Rhodamine 6 G aqueous solution of a finite concentration, at first D-Band grows gradually accompanied with the reduction of M-Band, but when the quantity of the added PVSK reaches a certain critical value, then M-Band begins to grow again, though the turning point is not so sharp and varies according to the dye concentration. Some examples are shown in Fig. 1.

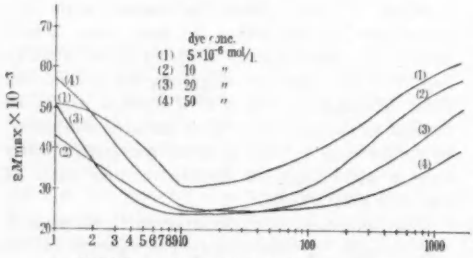

Fig. 1.—Change of molar extinction coefficient of M-band max. by P.V.S.K.

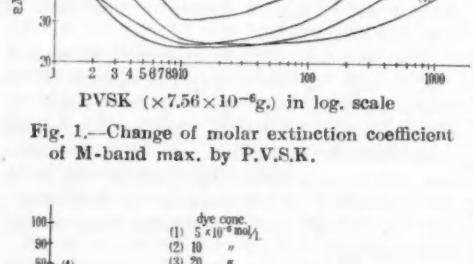

Fig. 2.—Change of relative fluorescence intensity (F'/F) by P.V.S.K.

Such behaviour is always observed in any concentration of dye between 5×10^{-6} mol./l. and 5×10^{-5} mol./l. In addition, it is to be noted that the position of M-Band does not change at all by the addition of PVSK and D-Band shows only a very feeble shift toward the shorter wave length.

(d) With the addition of PVSK the intensity of fluorescence decreases gradually at first until the concentration reaches the same critical value as the absorption, and beyond the critical concentration, the intensity gradually recovers with the further addition of PVSK. Some examples are shown in Fig. 2.

Discussion

As for the absorption spectrum of the aqueous Rhodamine 6 G solution, Levshin[4] performed a quantitative study and analysed the result on the assumption that the spectral change with concentration depends upon the monomer-dimer ratio determined by the mass action law. He also measured the intensity of fluorescence and could roughly account for the concentration quenching as a result of the dimerisation on the assumption that only monomer can fluoresce while dimer cannot.

Our results for the aqueous dye solution (with no PVSK added) are quite in accord with his.

Now when PVSK is added, such behaviour as mentioned above (cf. c and d) is observed and these results can be explained very well by the following model.

"When PVSK is added to the aqueous solution of dye, the dye ion concentrates in the neighborhood of PVSK molecule (or it may conventionally be stated, that the dye ion is adsorbed on PVSK), where the association equilibrium shifts greatly toward the dimer; but the optical properties for both monomer and dimer such as electronic states related to the light absorption, absorption coefficient and efficiency of fluorescence are supposed to be influenced scarcely at all by this adsorption". According to this model, it goes without saying that we can explain the observed decreases both in M-Band and in fluorescence intensity when a small quantity of PVSK is added; while the phenomena of recovery both in M-Band and in fluorescence when enough PVSK is added can be interpreted as follows.

When the added quantity of PVSK reaches a certain value (which depends on the concentration of dye), the dye concentration on the surface of PVSK will begin to decrease since the amount of dye in the whole system remains constant; then the association equilibrium will become shifted back again toward the monomer and the concentration of the monomer in the whole system increases, which causes M-Band and the fluorescence intensity to recover.

Thus Rhodamine 6 G-PVSK system seems to belong to the ideal case (2) described in the introduction.

Though the above qualitative explanation is very reasonable, there might be some other ways

of explanation. For example, if the interaction between PVSK molecules, in the region of high concentration, becomes so great as to change their aggregation in some way, this change of aggregation in PVSK might cause the adsorbed dye molecule to be detached back into the solution as monomer.

In connection with such a possibility the recent report of Lovelock[5] is to be noted. He studied the fluorescence in almost the same system as ours and observed the same phenomenon of recovery; he did not however explain it clearly and attributed it rather ambiguously to the ionic effect. He seems to be of the opinion that the dye ion when attached to the high polymer loses its tendency for fluorescence. If this be true, the phenomenon of recovery must be exclusively due to the detachment of the dye ion, which will take place only when some remarkable change in the state of aggregation occurs in PVSK. This is very improbable in the case of PVSK, but, in order to confirm this more definitely, we have further examined our model more quantitatively in two ways as follows.

(1) First, on the assumption that the present system is the ideal case (2) the molar fraction of the monomeric ion in the whole system can be calculated from the following two equations ((1) and (2) respectively refer to the absorption data and fluorescence data).

$$x_M(A) = (2\varepsilon - \varepsilon_D)/(2\varepsilon_M - \varepsilon_D), \qquad (1),$$

$$x_M(F) = \frac{(F/c)(F'/F)}{(F/c)_{c\to 0}}. \qquad (2).$$

In equation (1), ε is the molar extinction coefficient at the peak of M-Band in any system, ε_M and ε_D are respectively that of monomer and dimer at the same position, which can be obtained when the concentration of dye is extrapolated to zero or infinite.

In equation (2), F is the intensity of fluorescence when the dye concentration is c and no PVSK is added, while F' is the same quantity when some PVSK is added at the same concentration of dye. The values of F'/F and $(F/c)/(F/c)_{c\to 0}$ can be obtained from the experiment and $x_M(F)$ can thus be calculated.

We have calculated $x_M(A)$ and $x_M(F)$ in the whole range of concentrations of dye and PVSK. The results can be summarised as follows.

When the concentration of dye is 5×10^{-6}mol./l., $x_M(A)$ and $x_M(F)$ coincide almost completely in the range from 7.56×10^{-6} g. to $2000\times7.56\times10^{-6}$ g. of the added PVSK, as shown in Table 1. As the dye concentration is increased, the ratio $x_M(A)/x_M(F)$ gradually increases to some extent*; the result suggests the existence of some other effects of the high polymer on fluorescence, which are not taken account of in our model. In spite of such a discrepancy, the values of $x_M(A)$ and $x_M(F)$ change almost in parallel over a wide range of concentrations both of the dye and PVSK.

Table 1

$x_M(A)$ and $x_M(F)$ for various quantities of added PVSK.

dye conc. (mol./l.)	conc. of PVSK (unit $=7.56\times10^{-6}$g.)	$x_M(A)$	$x_M(F)$
5×10^{-6}	0	0.95	0.87
	1	0.56	0.55
	2	0.52	0.46
	4	0.44	0.47
	10	0.24	0.21
	25	0.26	0.21
	125	0.39	0.36
	200	0.48	0.44
	1000	0.68	0.58
	1500	0.76	0.77
	2000	0.79	0.56
10×10^{-6}	0	0.94	0.79
	1	0.44	0.34
	2	0.34	0.26
	10	0.22	0.11
	25	0.17	0.12
	125	0.27	0.17
	250	0.39	0.26
	500	0.44	0.37
	1000	0.61	0.39
	1500	0.62	0.54
	2000	0.70	0.46

Those results including Table 1 are considered to support our model quite well.

(2) Next, we have tried, on the basis of our model, to derive a theoretical relation between $x_M(A)$ on one side and the change of concentrations both of dye and PVSK on the other, in order to examine more precisely whether the experimental results can be reconciled with the model.

For this purpose, we have further assumed such a simple model of adsorption as the following; the adsorption equilibria are supposed to be established separately for monomer and dimer according to the following two equations.

$$C_M' = k_M C_M, \qquad (3),$$

$$C_D' = k_D C_D. \qquad (4).$$

where C_M and C_D are, respectively, the concentrations of monomer and dimer in the solution (in mol./l.) while C_M' and C_D' are the concentrations of the two species on the surface of the adsorbent (i.e. PVSK) (in mol./cm^2.).

In addition to these two equations, the mass action law obviously holds in the solution

$$C_M^2/C_D = K, \qquad (5),$$

We put further

(5) J. E. Lovelock, *J. Chem. Soc.* **1951**, 115-20.

* Levshin (4) has observed such a discrepancy even in the simple aqueous solution of Rhodamine 6 G.

P: number of grams of PVSK
S: the area of adsorbent per 1 g. (in cm.^{2})
V: the volume of solution (in cm.^{3})
C_0: the analytical concentration of the dye (in mol./l.)

then, starting from the above three equations (3) (4) (5) we can easily derive the following equation

$$\frac{y^2}{ZK} = \frac{(1+a_M P)^2}{1+a_D P}, \tag{6}$$

where y and Z are concentrations of the monomer and dimer, respectively, in the whole system which are given by equations (7) and (8)

$$y = \frac{C_M(V+k_M SP)}{V}, \tag{7}$$

$$Z = \frac{C_0 - y}{2}, \tag{8}$$

a_M and a_D are the quantities given as follows

$$a_M = k_M S/V$$
$$a_D = k_D S/V.$$

It is remarkable that the equation (6) has the peculiar character that y^2/ZK is a universal function of the quantity of added PVSK alone, irrespective of the dye concentration. If this relation really holds between the experimentally obtained y^2/ZK values and P, we may conclude the correctness of our model with much confidence.

Now the value of y can be calculated from the relation $y = c_0 x_M(A)$* with the use of the experimentally obtained $x_M(A)$ value, and Z-value is also easily calculated by the relation (8). Thus, we have tested the applicability of the relation (6) for the experimental data. It turned out that they obey the relation (6) quite well throughout the whole range of experiment covering from 5×10^{-6} mol./l. to 5×10^{-5} mol./l. for dye concentration and from 7.56×10^{-6} g. to 15.17×10^{-3} g. for PVSK. Especially, when P is large, the theoretical requirement is satisfied almost quantitatively; in this region, the equation (6) is put approximately as follows,

$$\frac{y^2}{ZK} \approx \frac{a_M^2}{a_D} P + 2\frac{a_M}{a_D}, \tag{9}$$

and the single universal linear relation must hold between y^2/ZK and P irrespective of the dye concentration. The experimental data have proved to satisfy this condition almost completely as shown in Fig. 3.**

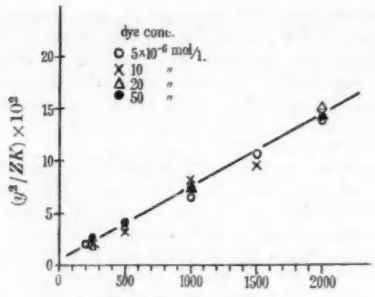

Fig. 3.—$(y^2/ZK)\sim P$ diagram for various dye concentrations.

In the opposite extreme case where the quantity of PVSK is small, (6) becomes approximately as follows

$$\frac{y^2}{ZK} \approx \frac{1}{1+a_D P} \tag{10}$$

In this region, the situation is not so good; at the fixed P-value, the experimental y^2/ZK values for the different dye concentrations differ a little from one another, though, for each dye concentration, the variation of the value y^2/ZK against P conforms with the above relation. This disagreement may, however, be attributed to the inadequacy of the equations (3) and (4) in this region. For, when the dye concentration is moderate and the quantity of PVSK is very small, the adsorption is more or less in the neighbourhood of saturation, and it may be a better approximation to put

$$C_M' = 0, \quad C_D' = \text{const}$$

instead of (3) and (4). Then the equation (10) becomes

$$\frac{y^2}{ZK} = \frac{1}{1+\dfrac{C_D' SP}{C_D V}}, \tag{11}$$

which agrees with the experimental results at least qualitatively. With (9) and (10) or (9) and (11), we can estimate the value of a_M and a_D as follows

$$a_M \simeq 1.6\times10^3$$
$$a_D \simeq 1.3\times10^5.$$

Therefore

$$k_M/k_D = 1/100.$$

Thus we can conclude, on the basis of the ideal case (2), that when the dimer ion is adsorbed on PVSK about 100 times more than the monomer, the change of absorption spectrum such as experimentally observed can be explained almost quantitatively.

* For some reasons x_M (A) is more reliable than x_M (F).

** Thus, in this region are approved not only our proposition that the present system of metachromasy is the ideal case (2), but also the simplified model of adsorption (equation (3) and (4)).

Conclusion

Two ideal cases for metachromasy were proposed: (1) one in which the effect is simply due to the change of the electronic state in the dye ion as a result of the interaction between the dye ion and metachromatic molecule, (2) the other in which the effect is simply due to the change of aggregation caused by the adsorption of the dye ion on the metachromatic substance. Two such effects are considered to be superposed in a general case. Rhodamine 6G-PVSK system can be explained almost quantitatively as a second ideal case.

The full account of the experimental data and the extensive discussion including other experimental results will be published in J. Inst. Polytech. Osaka City University.

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The Iodine Reaction of Rare Earth Elements. II.* Colorimetric Determination of Acetate Ions by the Iodine Reaction of Rare Earth Elements

By Kenjiro KIMURA, Nagao IKEDA and Masayasu NOMURA

(Received June 28, 1952)

It has long been known that basic lanthanum acetate shows a blue color reacting with iodine[1]. Krüger and Tschirch[2] applied this color reaction to the detection of acetate or lanthanum ions and reported its relatively high sensitivity. On the other hand, the application of this reaction to the quantitative analysis has long been the problem left to be solved. However, Hutchens and Kass[3] reported in their recent publication that successful results could be obtained on the microdetermination of acetate ions by this reaction.

The present authors[4] already noticed that similar color reactions occur when the basic acetate of praseodymium, neodymium or samarium reacts with iodine under the suitable conditions. In the present paper, they confirmed the method of Hutchens and Kass, then examined the possibility for the application of the corresponding reactions of praseodymium and neodymium to the same purpose.

Experimental

Materials.—The purity of the salts of lanthanum,[5] praseodymium[6] and neodymium[7] used was examined by the X-ray spectroscopic method. These salts are sufficiently pure for the practical use.

Use of Basic Lanthanum Acetate.

1. Development of the Color.—In a 5 ml. glass-stoppered test tube, put 1 ml. of standard solution of acetate ions[8], 1 ml. of lanthanum nitrate solution[9], 1 ml. of 0.1 N ammonia[10] and 1 ml. of 0.02 N iodine-potassium iodide solution. Heat the stoppered tube in boiling water for five minutes[11]. By this procedure, the color of the

* Previous paper: Kimura and Ikeda, This Bulletin, **21**, 19 (1948).

(1) Damour, *Compt. rend.*, **43**, 976 (1856).

(2) Krüger und Tschirch, *Ber.*, **62**, 2776 (1929).

(3) Hutchens and Kass, *J. Biol. Chem.*, **177**, 571 (1949).

(4) Kimura and Ikeda, This Bulletin, **21**, 19 (1948). They also observed that basic propionate of lanthanum, praseodymium or neodymium also shows a blue color reacting with iodine.

(5) Lanthanum oxide, commercially supplied in Japan, was purified by the Prandtl's fractional precipitation method; cf. Prandtl und Losch, *Z. anorg. allgem. Chem.*, **127**, 209 (1923).

(6) Praseodymium oxide of the Auer-Gesellschaft was used.

(7) Neodymium oxide of the Auer-Gesellschaft was used.

(8) The standard solution was prepared as follows: dissolve 2.226 g. sodium acetate ($CH_3COONa \cdot 3H_2O$) in water and make the total volume 1 l. 1ml. of the solution corresponds to 1.00 mg. CH_3COOH.

(9) 1 ml. of the solution corresponds to 5.0 mg. of lanthanum.

(10) The pH value of mixture of 1 ml. of lanthanum nitrate solution and 1 ml. of 0.1 N ammonia is about 8.8. According to Hutchens and Kass, the pH value of this mixture must lie between 8.3 and 8.5.

(11) Heating time less than fifteen minutes does not affect the coloration.

solution becomes yellowish green to greenish blue according to the amounts of acetate ions present.

The absorption curve for the solution with color developed as above, measured by the Pulfrich photometer, is shown in Fig. 1. The absorption at 430 mμ[12] evidently results from the light absorption by excess iodine, and the absorption maximum at 610 mμ[13] is attributed to that by the iodine-basic lanthanum acetate compound. For the actual use, however, the authors selected the filter S66 because of its much lower absorption against excess iodine.

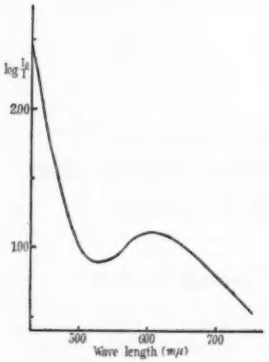

Fig. 1.—Absorption curve for the iodine-basic lanthanum acetate solution.
(0.5 mg. CH_3COOH/4 ml., Cell: 5 mm.)

The color thus obtained is very stable, and shows virtually no change even after 24 hours' standing.

2. Calibration Curve.—The solutions containing various amounts of acetate ions were treated in the way mentioned above, and the relation between the concentration of acetate ions and optical density was investigated. In Fig. 2 data obtained are presented graphically, showing the relation between optical density at 660 mμ and the amounts of acetate ions.

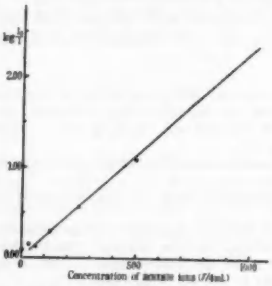

Fig. 2.—Calibration curve for basic lanthanum acetate.
(Filter: S66, Cell: 5 mm.)

As is evident from the figure, the Beer's law is adaptable in the concentration range of acetate ions between 60 γ and 500 γ (as CH_3COOH)[14] per 4 ml., i. e. the total volume of the colored solution. In this concentration range, the colored solution is clear, and the colorimetric determination of acetate ions by the Pulfrich photometer is possible.

When the concentration of acetate ions is smaller than 60 γ per 4 ml., the color caused by iodine reaction of basic lanthanum acetate is no longer observed and the resulting solution partly shows colloidal turbidity[15]. The limit of identification for acetate ions by this method is 60 γ per 1 ml. of the original sample solution.

When the concentration is greater than 500 γ per 4 ml., deviations from the Beer's law occur.

3. Effect of Other Ions Present.—As for the effect of other ions present and the method for removing the interfering ions in this procedure, it was already studied in detail by Hutchens and Kass[16], and their methods seem to be valid.

In addition, citrate ions severely interfere with this color reaction.

Use of Basic Praseodymium Acetate.

It has been believed that the color reaction between iodine and basic acetates of rare earth elements is specific to lanthanum. However, Kimura and Ikeda[17] noticed that besides the basic acetate of lanthanum, those of praseodymium, neodymium and samarium take on an intense indigo color when properly treated with iodine. It allows the prediction that in such cases the colorimetric determination of acetate ions might be possible as in the case of lanthanum.

1. Development of the Color.—Although the acetate solution was treated under the same condition as in the case of lanthanum except the use of praseodymium nitrate instead of lanthanum nitrate, no transparent colored solution suitable for the quantitative analysis could be obtained.

Since it was already pointed out in the previous paper that the amount of ammonia used always plays an important role in the iodine reaction of rare earth elements, the authors tried the experiment with various concentrations of acetate ions and ammonia. The concentration of acetate ions should be high and that of ammonia should be low for the present purpose.

1 ml. of standard solution corresponding to 5 mg. acetate[14] was treated with 1 ml. of praseodymium nitrate solution[18], 1 ml. of ammonia of various concentrations and 1 ml. of 0.02 N

(12) It corresponds to the absorption of the filter S43.
(13) It corresponds to the absorption of the filter S61.
(14) The amount of acetate ions is represented as γ or mg. CH_3COOH in this paper.
(15) In the blank test, i. e. when no acetate ion is present, the resulting solution also shows colloidal turbidity to some extent.
(16) op. cit.
(17) op. cit.
(18) 1 ml. of the solution corresponds to 11.4 mg. of praseodymium.

iodine-potassium iodide solution in a 5 ml. glass-stoppered test tube. After 15 minutes'[19] heating in boiling water, the color of the resulting solution was observed. The results are listed in Table 1. It is revealed that the use of ammonia of 0.04—0.06 N gives a transparent colored solution suitable for the colorimetric determination. The pH values in this case are much smaller than those in the case of lanthanum.

Table 1

Concentrations of Ammonia (N)	Coloration and Precipitation	*p*H Values of the Mixed Solution of 1 ml. of Praseodymium Nitrate and 1 ml. of Ammonia
0.02	No coloration or precipitation	—
0.03		6.0
0.04	Transparent green solution	6.3
0.045		6.5
0.05		6.6
0.06		7.0
0.07	Blue precipitation	7.4
0.08		—

2. Calibration Curve.—The solutions containing various amounts of acetate ions were treated in the way mentioned above using 0.045 N ammonia, and the relation between the concentrations of acetate ions and optical density was checked by the Pulfrich photometer. The results are illustrated graphically in Fig. 3 showing optical density at 660 mμ versus the amount of acetate ions.

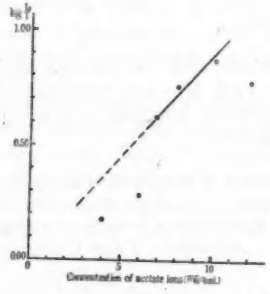

Fig. 3.—Calibration curve for basic praseodymium acetate.
(Filter: S66, Cell: 5mm.)

In the range of concentrations of 5—10 mg. acetate[14] per 4 ml., the transparent, yellowish green—bluish green solution was obtained. Beer's law is approximately adaptable in the range of 7—10 mg. per 4 ml., although the points on the graph are somewhat fluctuating. In smaller concentrations of acetate than 4 mg. per 4 ml., no coloration of the iodine reaction is observed. When it is larger than 10 mg. per 4 ml., blue precipitation occurs, and the colorimetric determination is no longer possible.

As is shown above, the sensitivity of this reaction in the case of praseodymium is much inferior to that in the case of lanthanum. Therefore, lanthanum nitrate should be used for the determination of acetate ions.

Use of Basic Neodymium Acetate.

The use of neodymium salt for the purpose of the determination of acetate ions was then investigated.

1. Development of the Color.—The mixture of 1 ml. of standard solution corresponding to 5 mg. acetate[14], 1 ml. of neodymium nitrate solution[20], 1 ml. of ammonia of various concentrations and 1 ml. of 0.02 N iodine-potassium iodide solution taken in a 5 ml. glass-stoppered test tube was heated in boiling water for ten minutes. Then, the color of the solution was observed. The results are shown in Table 2. The suitable range of concentrations of ammonia is 0.02—0.03 N, and the corresponding pH values are much smaller than those in the case of lanthanum and are almost similar to those in the case of praseodymium.

Table 2

Concentration of Ammonia (N)	Coloration and Precipitation	*p*H Values of the Mixed Solution of 1 ml. of Neodymium Nitrate and 1 ml. of Ammonia
0.01	No coloration or precipitation	5.7
0.02	Transparent green solution	6.0
0.03		6.4
0.04	Blue precipitation	6.8
0.05		—

2. Calibration Curve.—The solutions containing various amounts of acetate ions were treated in the way mentioned above using 0.02 N ammonia. The relation between the concentrations of

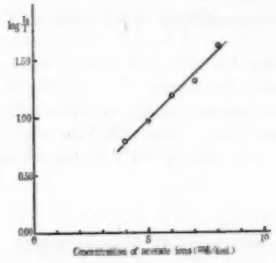

Fig. 4.—Calibration curve for basic neodymium acetate.
(Filter: S66, Cell: 5 mm.)

(19) In the case of praseodymium, fifteen minutes' heating is necessary to complete the color reaction, while five minutes' heating is sufficient in the case of lanthanum.

(20) 1 ml. of the solution corresponds to 7.0 mg. of neodymium.

Table 3

	Concentration of Ammonia used	*p*H Values of the Mixture of Nitrates and Ammonia	Concentration Range Available for the Colorimetric Determination	Limit of Identification
Lanthanum	0.1 N	8.8	60—500 γ/ml.*	60 γ/ml.*
Praseodymium	0.045 N	6.5	7—10 mg./ml.	4 mg./ml.
Neodymium	0.02 N	6.0	4— 8 mg./ml.	4 mg./ml.

* The volume is taken for the original sample solution.

acetate ions and optical density was checked by the Pulfrich photometer. Data are shown graphically in Fig. 4 representing optical density at 660 mμv ersus the amounts of acetate ions. In the concentration range of 4—8 mg.[14], Beer's law is adaptable. At smaller concentrations of acetate ions than 4 mg. per 4 ml., no coloration of the iodine reaction is observed. When it is larger than 8 mg. per 4 ml., blue precipitation occurs and the colorimetric determination is no longer possible.

The sensitivity of this reaction in the case of neodymium is much inferior to that in the case of lanthanum. It rather resembles to that in the case of preseodymium.

Conclusion

It is evident that the color reaction between iodine and the basic acetate of praseodymium or neodymium is applicable to the colorimetric determination of acetate ions as in the case of lanthanum. There are, however, partial differences between each case of them in the suitable concentration of ammonia and the sensitivity of the reaction. These are briefly tabulated in Table 3 for comparison.

The concentration of ammonia and the pH value suitable for quantitative analysis decrease in the order of lanthanum, praseodymium and neodymium, i. e., with the decrease of the basicity of the elements.

As for the sensitivity of the reaction for acetate ions, it is especially good in the case of lanthanum. In the case of praseodymium and neodymium, it resembles each other and are much inferior to that in the case of lanthanum.

Summary

The application of the color reaction between basic lanthanum acetate and iodine to the quantitative analysis has long been the problem left to be solved. Recently, hawever, Hutchens and Kass succeeded in application of this color reaction to the micro-determination of acetate ions with good results.

The present authors examined this method and confirmed that satisfactory results were obtained in its application. In addition, the authors found that the corresponding reactions for praseodymium and neodymium were applicable, too, to the same purpose, although in these cases the sensitivity was not so good as that in the case of lanthanum.

The authors wish to express their hearty thanks to Prof. Kin-ichiro Sakaguchi for his kind suggestions rendered during the course of this work.

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Separation of the Components of Atmospheric Salt and their Distribution (Continued)

By Tadashiro KOYAMA and Ken SUGAWARA

(Received July 7, 1952)

Introduction

In the previous paper[1] it was shown that due to evaporation, the spray particles of the sea water in the air, separate into at least two kinds of daughter particles; the one, hygroscopic in nature and consisting mainly of sodium chloride, and the other, crystalline in nature and consisting mainly of calcium sulphate*. The latter, being more stable, continues to remain longer in the air and tends to be carried horizontally towards inland or to be raised higher vertically. Thus the distribution of several components of the atmospheric salt are so arranged that the ratios Ca/Cl, Mg/Cl and SO_4/Cl grow larger as we move towards inland or go higher from sea level.

The writers continued the study in a small island "Sugashima" (Fig. 1), located in Ise Bay, about 4 km off Toba, Mie-Prefecture, and the situation in a limited area close to the beach made it possible for them to obtain considerable new information, which will be given below.

The study was carried out as follows: Seven stations were chosen, different in height, starting from the sandy beach "Shirasaki" up to the summit of Mount Ôyama with a height of 236.6 m. At each station except Shirasaki the washings of pine needles were collected

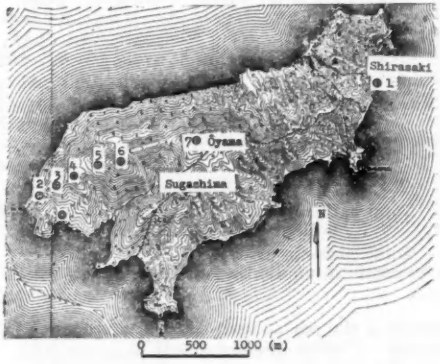

Fig. 1.
⊕···Stations where the samples were collected.
◎···Marine Biological Laboratory attached to Nagoya University.

according to the procedure which was given in the foregoing paper[1]. At Shirasaki, a bare sandy area with no pine trees, a cotton gauze, spanning a metallic frame, was fixed in the calm weather just above the sand so that it was exposed to the sea breeze. After 5 hours exposure the gauze was taken off to rinse with distilled water. In addition to the determination of Na, Mg, Ca, Cl, SO_4 of the washings of pine needles and the cotton gauze, we determined the total carbonic acid of the samples, collected on Dec. 18—19, 1949, where its ratio to chlorine was determined. Also the residual fraction of filtration of a number of the washings left on filter paper, was determined for Ca and Mg and their ratios to Cl were established. The results are given in Tables 1～4.

Results and Discussions

1. What was shown first was that the variation in the composition of the atmospheric salt was very evident already in the samples from the succeeding seven stations (See Table 1). This means that the fractional separation of the components of sea water begins to occur over the

(1) K. Sugawara, S. Oana, and Tadashiro Koyama: Separation of the Components of Atmospheric Salt and their Distribution, This Bulletin, **22**, No. 2, 47-52 (1949).

* It should be noted that a similar attempt to interpret the variation in the salt composition in rain water by the fractional segregation of the sea salt was already done by H. Matsui who assumed the segregated particles to act as condensation nuclei, thus causing the variation (*J. Meteor. Soc. Japan*, **22**, 2-12 (1944)). In the present paper, the writers deal on the one hand with the problem, and their conclusions are based upon observational and experimental firmer and more definite data, on the other hand they make it clear that the fractionation begins to occur as early as just after the spray is formed from the surface of the sea.

It should also be added that, according to the writers' view, salts are not only supplied to the rain water as condensation nuclei but a considerable amount of them is dissolved in it in its course of falling by washing after the drops are formed.

Table 1

Washings of Cotton Gauze and Pine Needles from 7 Stations, Sugashima, Different in Height and Distance from the Beach. (Nov. 13, 1948)

Ratio in Equivalent	Sea Water	Stations 1	2	3	4	5	6	7
SO_4/Cl	0.100_7	0.096_8	0.099_5	0.124_0	0.132_6	0.143_9	0.162_6	0.149_3
Na/Cl	0.860	0.829	0.819	0.848	0.860	0.845	0.845	0.853
Ca/Cl	0.037_9	0.041_2	0.061_6	0.065_5	0.071_8	0.074_6	0.105_6	0.099
Mg/Cl	0.195_1	0.198_6	0.196_9	0.198_4	0.208_4	0.223_9	0.236_6	0.224_7
Ca/SO_4	0.376_2	0.426	0.618	0.528	0.544	0.519	0.652	0.668
$\Sigma+/\Sigma-$	0.98_6	0.97_4	0.98_1	0.98_8	1.00_6	0.99_8	1.02_2	1.02_5

Table 2

The Total Carbonic Acid and its Ratio to Cl in the Washings of Pine Needles from Sugashima

	Sea Water	Stations 1	2	3	4	5	6
Cl (mg./l.)	184_{30}	215_9	725	733	$376._9$	$341._8$	561
Total carbonic acid (milli-equiv./l.)	3.63	0.56	0.35	0.61	0.38	0.47	0.93
Total carbonic acid/Cl (Ratio in equivalent) $\times 10^3$	0.69_8	0.9_2	1.7	2.9	3.6	4.9	5.9

surface of the sea as early as just after spray is formed. A fuller discussion will be given later.

2. The simultaneous determination of Cl and total carbonic acid (Table 2) shows that carbonates are important components of the atmospheric salt and their relative amount in it grows larger as we recede from the beach, a relation coming in harmony with a general trend of a relative increase of positive components, to negative ones as shown by $\Sigma+/\Sigma-$, the ratio of the sum of the equivalents of the positive components to that of those of the negative ones (Table 1). The increase of $\Sigma+/\Sigma-$ is not only evident in the case of the washings of pine needles on Sugashima, but also in sets of the comparison data of samples of rain water as well as of the pine needles between Sugashima, Nagoya and Matsumoto as given in Tables (Table 3 a, b). The relation is also true in the comparison of the ordinary rain-water, rain from thunderstorms and the rime water from Mt. Fuji (Table 3 c). The whole result tells that in addition to calcium sulphate, we must assume magnesium carbonate and particularly calcium carbonate as members of the stable segregates from the primary spray particle, which remain longer in the air and form predominant components of the atmospheric salt in the air in higher strata and over locations away from the sea beach.

The present view is supported by the determination of Mg and Ca in the residual fraction from filtration of the washings of pine needles which is assumed to consist mainly of carbonates. The result given in Table 4. suggests that actually Mg and Ca are the primary positive components of the carbonate in question and at the same time it shows that between two kinds of carbonates, calcium carbonate is more stable and its

Table 3

(a)

Ratio in Equivalent	Sea Water	Oridinary Rain Sugashima	Nagoya	Matsumoto
SO/Cl	0.1007	0.35	0.368	1.70
Na/Cl	0.860	0.85	0.882	0.91
Ca/Cl	0.0379	0.25	0.298	3.50
Mg/Cl	0.1951	0.23	0.291	0.66
Ca/SO_4	0.376	0.72	0.832	2.06
$\Sigma+/\Sigma-$	0.986	0.98	1.074	1.88

(b)

Ratio in Equivalent	Washings of Pine Needles Sugashima	Nagoya	Matsumoto
SO_4/Cl	0.17	0.72	1.82
Na/Cl	0.83	0.85	1.58
Ca/Cl	0.09	0.55	4.13
Mg/Cl	0.22	0.27	1.26
Ca/SO_4	0.53	0.76	2.27
$\Sigma+/\Sigma-$	0.97	0.97	2.47

(c)

Ratio in Equivalent	Ordinary Rain	Thunder-storm	Rime from the Summit of Mt. Fuji
SO_4/Cl	0.368	3.24	1.00
Na/Cl	0.882	2.43	1.09
Ca/Cl	0.298	2.19	1.90
Mg/Cl	0.291	0.63	0.40
Ca/SO_4	0.832	0.676	1.90
$\Sigma+/\Sigma-$	1.07_4	1.23_6	1.69

relative amount increases rapidly from the beach towards the summit of Mt. Ôyama.

Table 4

Acid Soluble Components in the Residual Fractions of the Washings of Pine Needles from Sugashima

Ratio in Equivalent $\times 10^2$	1	2	3	4	5	6
Ca/Cl	0.002	—	0.746	0.860	1.164	2.65
Mg/Cl	0.357	—	0.221	0.760	0.982	1.174

3. In the previous paper, the writers tried to picture a rough image of the processes of the fractionation of the spray of sea water which occasion the regular distribution of the components of atmospheric salt. The result, reported in the present paper, forces us to modify the picture and elaborate it in its detail to some extent. Namely in the foregoing rough picture the writers assumed that the primary particle of the spray of sea water separates into two kinds of secondary particles; the one, consisting mainly of Ca and SO_4 and more stable, remains longer in the air, and the other, consisting mainly of sodium chloride and less stable, is fated to fall down from the air earlier. The later knowledge, obtained above, affords reason to assume calcium carbonate as well as magnesium carbonate as stable segregates other than sulphates. Secondly the segregation processes must be assumed to begin to occur as early as just after the spray is formed due to wave crushing and while it is suspended in the air unstable segregates fall down back to the sea surface below, leaving a mass of particles whose composition is already quite different from that of the original sea water.

4. Further details of the segregation lie still beyond our knowledge; however, the writers may be allowed to try to draw some imaginary picture of it. Thus let us quote the old experiment by Usiglio[2] on laying down of salts from the sea water when it is fated to slow evaporation. According to him, at the first stage of concentration, i. e., till the time when 1 l. of sea water is concentrated to 533 cc., about 0.0642 g. of $CaCO_3$ is laid down and at the second stage of concentration to 112 cc., 1.466 g. of $CaSO_4 2H_2O$ with a smaller amount of $CaCO_3$ separates, leaving a brine containing certain amounts of Na, Mg, Ca, Cl and SO_4. Thus we can naturally assume a similar segregation of salts to occur on the spray in suspension, giving rise to the particles of calcium carbonate and gypsum, leaving brine particles. The particles differ in stability and the greater part of the brine particles which are the least stable, will fall down to the sea surface earlier while the particle of $CaCO_3$, probably the most stable, will remain in suspension in the largest proportion. When the composite mass of particles, thus formed, is carried up to the beach and touched by a cotton gauze or pine needles, it is quite natural to assume that a second selective adhesion occurs depending upon the different adhesivity of the individual components. Anyhow we can try to test whether it is possible to obtain the composition of the washings-samples by an appropriate combination of these three kinds of particles, i. e., (a) $CaCO_3$, (b) $CaSO_4 2H_2O$ and (c) the residual brine. For example, let us try to compose the composition of the gauze washings, given in Column 3 of Table 1, by combination of 1 part of the salt in the brine (c), x part of chalk (a) and y part of gypsum (b)*.

Each fraction from 1 l. sea water contains the following amounts of component in equivalent.

	Na	Mg	Ca	Cl	SO_4	CO_3
Fraction (a)	—	—	0.00218	—	—	0.00218
Fraction (b)	—	—	0.0065	—	0.0065	—
Fraction (c)	0.518	0.111	0.003	0.595	0.045	—

Then the amounts of the individual components in the final composite are

Na 0.518
Mg 0.111
Ca .....0.003+0.00218x+0.0065y
Cl 0.595
SO_4.... ....0.045+0.0065y

Then, in order to obtain the value of y, the following equation is set up:

$$\frac{\text{Na}}{\text{SO}_4}=\frac{\text{Na}}{\text{Cl obs.}}\div\frac{\text{SO}_4}{\text{Cl obs.}}$$

By introducing the values obtained above and those given in Column 3 of Table 1,

$$\frac{0.518}{0.045+0.0065y}=\frac{0.829}{0.0968}.$$

Thus $y=2.38$ and consequently the amount of SO_4 is determined as 0.0605.

Next x can be evaluated similarly by assuming an equation

$$\frac{\text{Ca}}{\text{SO}_4}=\left(\frac{0.003+0.0155+0.00218x}{0.0605}\right)=(0.426)\text{obs.}$$

Thus $x=3.33$ and consequently Ca=0.0257

Summarizing the result, we can compare the values from direct observation of the ratios of individual components of the washings of the cotton gauze to those calculated from the model process here assumed above.

(2) *Annales chim. phys.*, 3rd Ser., **27**, 92, 172 (1849).

* For convenience the amount of $CaCO_3$, laid down accompanied by gypsum, was added to fraction (a) and Br calculated as an equivalent amount of Cl.

	Sea water	Cotton Gauze Observed	Cotton Gauze Calculated
Na/Cl	0.860	0.829	0.870
Mg/Cl	0.194_4	0.198_6	0.187_6
Ca/Cl	0.037_9	0.041_2	0.043_2
SO_4/Cl	0.100_7	0.096_6	0.101_6
Ca/SO_4	0.376_2	0.42_6	0.42_6
$\Sigma+/\Sigma-$	0.97_4	0.97_4	0.99_9

The conclusion is that the combination of 3.33 parts of fraction (a), 2.38 parts of fraction (b), and 1 part of fraction (c) yields an approximate composition of the washings of the cotton gauze, showing a rough stability sequence of the three fractions which were assumed above, and at the same time it suggests that the fractionation similar to the experiment by Usiglio or something like it, actually occurs on the spray in the air close to the surface of the sea.

No doubt, the treatment above is too easy and arbitrary to explain the supposed complexity of the phenomenon in question. It was simply aimed at building up some concrete broad image along which further studies could be extended. Our knowledge, hitherto obtained, gives a concrete reason to consider magnesium carbonate as another independent fraction and fraction (c) must be divided into several subfractions. Otherwise the variability of the ratio Na/Cl can not be explained. However it will go too far, we believe, for us to discuss the matter further and to try to picture a fuller detail in the process based upon the insufficient knowledge that we now have.

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Electrolytic Behavior of Elements of the Group VIa in the Periodic System. I. Potentiometric Studies on the Chromate, Molybdate and Tungstate Ions

By Kuan PAN and Tong Ming HSEU

(Received April 11, 1952)

Introduction

It has been known that molybdic and tungstic acids form well-defined soluble normal salts similar to those of chromates, but they do not resemble chromic acid in some electrolytic behaviors. In their abnormalities, however, molybdic and tungstic acids bear to one another remarkable similarities, such as the formation of poly-anions.

Several investigations on the formation of these poly-anions of molybdate and tungstate in aqueous solutions have been published since the beginning of the twentieth century.(1)~(8) These investigators suggested that, beside the normal ion MoO_4^{--}, various kinds of poly-anions may be formed in aqueous solution at varying dilutions and at different *p*H ranges. Thus the possible existence of $H_3Mo_6O_{21}^{3-}$, $HMo_6O_{21}^{5-}$, or $O(MoO_3)_n^{2-}$, has been proposed by estimating the ratio, Na_2O/MoO_3, from the experimental results of conductometric and potentiometric titrations of molybdate and tungstate with strong or weak acid. On account of the complexity of the relation of equilibria between these poly-anions, or due to the experimental difficulties, some of the conclusions seem to be overstrained or presumptive and further verifications seem to be left for the present investigation.

The present and subsequent papers in this

(1) H. T. S. Britton and W. Leslie, *J. Chem. Soc.*, **1927**, 147.
(2) H. T. S. Britton and M. L. German, *J. Chem. Soc.*, **1930**, 1249; **1931**, 709.
(3) R. H. Vallance and E. G. K. Pritchett, *J. Chem. Soc.*, **1931**, 1421; **1934**, 1596.
(4) G. Jander, K. F. Jahr and W. Heukeshoven, *Zeit. anorg. allgem. Chem.*, **187**, 60, 129 (1930); **194**, 383 (1930).
(5) R. A. Robinson and D. A. Sinclair, *J. Chem. Soc.*, **1934**, 642.
(6) H. Brintzinger and C. Ratanarat, *Zeit. anorg. Chem.*, **224**, 97 (1935).
(7) E. Buchholtz, *Zeit. anorg. allgem. Chem.*, **244**, 149, 168 (1940).
(8) G. Carpeni, *Bull. soc. chim. France*, **1947**, 484, 490, 492.

series have attempted to verify the existence of these poly-anions from results obtained by means of potentiometric and conductometric measurements as well as by studies of the Raman spectra or absorption spectra of these solutions. The purpose of the present paper which reports the results of potentiometric measurements is three fold: first, to obtain more accurate data on the *p*H values of the aqueous solutions of molybdates and tungstates as well as chromates by means of a glass electrode and to ascertain the existence of dimolybdate and ditungstate ions, $X_2O_7^{--}$, from the *p*H changes governing the hydrolytic process of these salts; second, to verify the dissimilarities in electrolytic behavior between chromate and molybdate or tungstate by measuring the *p*H values at varying dilutions and checking the differential quotients, $dp\mathrm{H}/d\log C$, which will also be expected from the theoretical calculation; third, to ascertain the existence of poly-anions at varying *p*H values by means of potentiometric titration of sodium molybdate or tungstate with hydrochloric acid.

Experimental

(1) **Materials.**—Conductivity water having a specific conductivity of 1.6 to 2.4×10^{-6} mho was prepared by refluxing and distilling water over potassium permanganate with sulfuric acid and then redistilling over barium hydroxide in pyrex glass apparatus.

Reagent grade hydrochloric acid was distilled twice. The constant boiling fraction was diluted to a desired concentration and used for the potentiometric titrations.

Reagent grade sodium molybdate and tungstate were recrystallized twice from the conductivity water and heated at 100°C. for two hours.

Potassium molybdate and tungstate were obtained by dissolving 1 mol. each of extra pure molybdic acid and tungstic acid, respectively, in a hot solution containing 2 mols. of potassium hydroxide. The salts separated on cooling were recrystallized, repeatedly, from the conductivity water and washed with 95% alcohol.

Sodium chromate and potassium chromate recrystallized twice from the conductivity water were used in this experiment.

The crystalline water as well as the composition of salts used in the present investigation was checked by the gravimetric method. The solutions were prepared, directly, by dissolving the salt in carbonate-free conductivity water and diluting to a desired concentration before each run.

(2) **Apparatus.**—A vacuum tube potentiometer, constructed in our laboratory, was used with a glass electrode. A vacuum tube, UX 54A,[9] made by Matsuda, Co. in Japan was used in this circuit. The characteristics of the tube are shown as follows:

filament potential	2.0 volt
plate potential	6.0 volt
screen grid potential	4.0 volt
control grid potential	4.0 volt
filament current	0.205 A.
plate current	40 μA.
screen grid current	297 μA.
control grid current	2×10^{-14} A.
mutual conductance	22 $\mu\Omega$

The working circuit is shown schematically in Fig. 1.

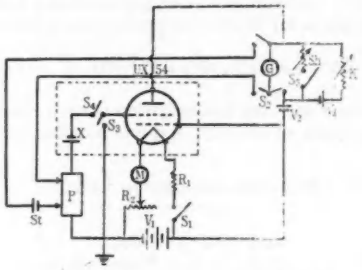

Fig. 1.—The working circuit of the vacuum tube potentiometer.

The component parts of the meter are given here for reference.

V_1: 6 volt battery
V_2: 3 volt battery
V_3: 1.5 volt battery
R_1: 10 ohm rheostat
R_2: 50 ohm rheostat
20,000 ohm rheostat
K: 3,000, 1,500 and 200 ohms variable resistances
S_1, S_2: switches
S_2, S_3, S_4: three pole three throw switches
Sh: galva shunt
G: galvanometer
M: milliammeter
X: glass electrode cell
P: Leeds and Northrup potentiometer
St: standard cell

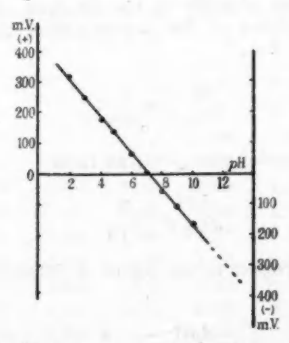

Fig. 2.—Calibration curve of the glass electrode.

(9) Yoshimura, This bulletin, **12**, 359, 443 (1937).

The glass electrode was checked frequently against the Clerk-Lubs series buffer solutions. The calibration curve plotted e. m. f. vs. the pH is indicated in Fig. 2. The quantitative relation between e. m. f., E, observed, and the pH value is formulated as

$$E=0.43-0.0001983\,T\,p\mathrm{H}$$

Results and Discussion

(A) Hydrolyses of tungstate, molybdate and chromate.

When a salt of a weak acid dissolves in aqueous solution, the hydrolysis of anions reaches a definite equilibrium for which the generalized reaction is

$$nA^{a-}+mH_2O \rightleftarrows pB^{b-}+qOH^- \qquad (1)$$

and when we take concentration of each constituent in place of activity, in dilute solution, putting

$$[A^{a-}]=C(1-x),\ [B^{b-}]=\frac{p}{n}Cx,$$

$$\text{and } [OH^-]=\frac{q}{n}Cx,$$

where x is the degree of hydrolysis and C the concentration, the hydrolysis constant, K_h, may be given, as a first approximation, by the expression:

$$K_h=\frac{[B^{b-}]^{p/n}[OH^-]^{q/n}}{[A^{a-}]}=\frac{1}{C}\left(\frac{p}{q}\right)^{p/n}[OH^-]^{\frac{p+q}{n}}. \qquad (2)$$

Hence,

$$p\mathrm{OH}=-\frac{n'}{p+q}\left(\log K_h-\frac{p}{n}\log\frac{p}{q}\right)-\frac{n}{p+q}\log C$$

or

$$p\mathrm{H}=14+\frac{n}{p+q}\left(\log K_h-\frac{p}{n}\log\frac{p}{q}\right)+\frac{n}{p+q}\log C \qquad (3)$$

that is to say, a linear relationship should be held between pH and log C. Consequently, the differential quotient of the pH with respect to the logarithm of the concentration should be constant, i. e.,

$$\frac{dp\mathrm{H}}{d\log C}=\frac{n}{p+q}. \qquad (4)$$

In a special case, $p=1$, we have

$$\frac{dp\mathrm{H}}{d\log C}=\frac{n}{1+q} \qquad (4a)$$

or with respect to the degree of dilution, V, we obtain

$$\frac{dp\mathrm{H}}{d\log V}=-\frac{n}{1+q} \qquad (4b)$$

as proposed by P. Souchay[10].

According to equation (3) if we assume that the hydrolytic processes of normal molybdate and tungstate in dilute solution can be formulated as

$$2XO_4^{--}+H_2O \rightleftarrows X_2O_7^{--}+2OH^- \qquad (1a)$$

and the ionic hydration as well as the other poly-anions formation can be neglected in these cases, the values of solutions may be evaluated as

$$p\mathrm{H}=14+2/3(\log K_h+1/2\log 2)+2/3\log C \qquad (3a)$$

or

$$\frac{dp\mathrm{H}}{d\log C}=\frac{2}{3}$$

that is to say, the slope of the curve plotted pH vs. $-\log C$ should be $-2/3$.

In the same way, in the hydrolytic process of chromate, which has been assumed to follow the reaction

$$CrO_4^{--}+H_2O \rightleftarrows HCrO_4^-+OH^- \qquad (5)$$

instead of

$$2CrO_4^{--}+H_2O \rightleftarrows Cr_2O_7^{--}+2OH^- \qquad (6),$$

the slope of the curve should be $-1/2$ instead of $-2/3$.

As shown in figure 3, in the cases of molybdate and tungstate, linear relationships exist between pH and $-\log C$ from C=0.1 to 0.001 mol. and the slope of each curve is nearly equal to $-2/3$. Agreement between the calculated and the observed values is excellent. On the other hand,

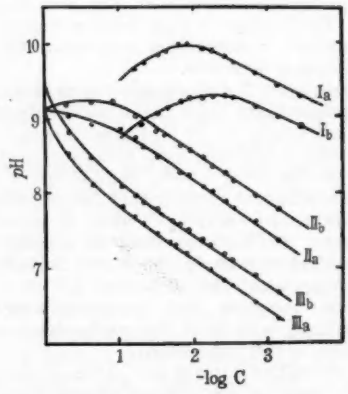

Fig. 3.—Hydrolyses of chromates, molybdates and tungstates.

Ia: Sodium chromate
Ib: Potassium chromate
IIa: Sodium molybdate
IIb: Potassium molybdate
IIIa: Sodium tungstate
IIIb: Potassium tungstate

(10) P. Souchay, *Bull. Soc. Chim. France*, **1948**, 433.

Table 1

*p*H Values of Chromates, Molybdates and Tungstates Solutions at Varying Dilutions at 30°C.

Dilution (liters/mol.)	$-\log C$	Na_2CrO_4	K_2CrO_4	Na_2MoO_4	K_2MoO_4	Na_2WO_4	K_2WO_4
10	1.00	9.49	8.72	8.88	9.18	7.84	8.10
16	1.20	9.63	8.86	8.72	9.00	7.67	7.99
20	1.30	9.71	8.90	8.58	8.98	7.60	7.91
32	1.51	9.83	9.07	8.50	8.82	7.45	7.80
40	1.60	9.89	9.12	8.45	8.77	7.39	7.71
64	1.81	9.97	9.21	8.31	8.65	7.24	7.58
80	1.90	10.00	9.26	8.26	8.59	7.18	7.52
128	2.11	9.93	9.28	8.10	8.46	7.05	7.37
160	2.20	9.90	9.30	8.04	8.38	6.97	7.33
320	2.51	9.73	9.28	7.80	8.17	6.75	7.12
640	2.81	9.59	9.16	7.60	7.98	6.53	6.90
1280	3.11	9.44	9.04	7.38	7.78	6.34	6.67
2560	3.41	9.27	8.88	—	—	—	—

in the case of chromate, the slope of the curve at lower concentrations agrees closely with $-1/2$. Although another slope having the opposite sign is also found at higher concentrations, it may probably be attributable to the effect of the secondary dissociation of bichromate ion.

The *p*H values of sodium chromate, molybdate and tungstate as well as potassium chromate, molybdate and tungstate solutions measured at varying dilutions are tabulated in Table 1. From these experimental values, we obtain a generalized empirical formula governing the *p*H values of the salt solutions with concentrations over the concentration range 0.1—0.001 mol. as follows:

$$pH = a + b \log C$$

where the constants a and b may be evaluated by the method of least squares from the experimental data. Their numerical values are summarized in Table 2.

Table 2

a and b for Chromates, Molybdates and Tungstates

Salt	a	b
Sodium Chromate	11.00	0.520
Potassium Chromate	10.50	0.485
Sodium Molybdate	9.60	0.712
Potassium Molybdate	9.85	0.675
Sodium Tungstate	8.50	0.701
Potassium Tungstate	8.80	0.683

Since the experimental results obtained by the hydrolysis of these salts are in good agreement with the theoretical values from equation (1a), the present investigation gives a confirmation for the existence of dimolybdate and ditungstate ions, $Mo_2O_7^{--}$ and $W_2O_7^{--}$ as well as bichromate ion, $HCrO_4^-$, in dilute solution, and it also gives a

Table 3

Hydrolyses of Chromates, Molybdates and Tungstates at Varying Dilutions (30°C.)

Dilution	Degree of Hydrolysis (X)						Hydrolysis Constant (K1)					
Liters/mol.	Na_2CrO_4 ($\times 10^2$)	K_2CrO_4 ($\times 10^2$)	Na_2MoO_4 ($\times 10^4$)	K_2MoO_4 ($\times 10^4$)	Na_2WO_4 ($\times 10^5$)	K_2WO_4 ($\times 10^5$)	Na_2CrO_4 ($\times 10^6$)	K_2CrO_4 ($\times 10^7$)	Na_2MoO_4 ($\times 10^{14}$)	K_2MoO_4 ($\times 10^{13}$)	Na_2WO_4 ($\times 10^{17}$)	K_2WO_4 ($\times 10^{18}$)
10	—	—	0.76	1.51	0.69	1.26	—	—	2.12	1.72	1.66	0.98
16	—	—	0.84	1.60	0.75	1.56	—	—	1.85	1.28	1.31	1.20
20	—	—	0.76	1.91	0.80	1.63	—	—	1.70	1.74	1.26	1.08
32	—	—	1.01	2.11	0.90	2.02	—	—	1.62	1.47	1.15	1.29
40	—	—	1.13	2.36	0.98	2.06	—	—	1.79	1.64	1.18	1.09
64	—	—	1.31	2.86	1.11	2.43	—	—	1.76	1.83	1.07	1.12
80	0.80	—	1.46	3.11	1.21	2.65	0.80	—	1.93	1.88	1.11	1.16
128	1.09	—	1.61	3.69	1.44	3.00	0.93	—	1.63	1.96	1.17	1.05
160	1.27	0.32	1.75	3.84	1.49	3.42	1.01	0.64	1.69	1.77	1.03	1.25
320	1.72	0.61	2.02	4.73	1.80	4.22	0.93	1.16	1.29	1.79	0.91	1.17
640	2.49	0.93	2.55	6.11	2.17	5.08	0.97	1.34	1.29	1.78	0.80	1.03
1280	3.53	1.10	3.07	7.71	2.80	5.99	0.97	0.94	1.13	1.79	0.86	0.84
2560	4.77	1.94	—	—	—	—	0.89	1.47	—	—	—	—
				Average.			0.93	1.11	1.67	1.72	1.13	1.11

confirmation for the similarity between the constitution of molybdate and tungstate as well as the dissimilarity between that of chromate and molybdate or chromate and tungstate.

Degrees of hydrolysis and the hydrolysis constants calculated from the *p*H values observed, by using equation (3a), are summarized in Table 3. Deviations at higher concentrations are not unexpected since activities have been ignored. On the one hand, from the facts that the degree of hydrolysis of molybdate is always greater than that of tungstate having the same concentration and the average value of the hydrolysis constant of the former is about a thousand times as great as the latter, as shown in Table 3, and also from the fact that *p*H values of the salt at the same dilution decrease in the order of chromate, molybdate and tungstate, as shown in figure 3, we may conclude that the strength of the acids increases with the atomic weights of these acidic metals, that is, in the order of chromic, molybdic and tungstic acids. On the other hand, by comparing the *p*H values of sodium tungstate with those of potassium tungstate, we find that potassium salt has greater *p*H values than those of the corresponding sodium salt, as in the cases of molybdates and tungstates. It may be attributable to the difference in the effect of the ionic size of the cations.

(2) Potentiometric titration of chromate, molybdate and tungstate with hydrochloric acid.

Data obtained by potentiometric titrations of normal salt solutions varying from 0.02 M to 0.1 M in molybdate ion or tungstate ion with 0.1 M hydrochloric acid at 30°C. are plotted as *p*H vs. the volume of 0.1 M hydrochloric acid added, as indicated in figure 4.

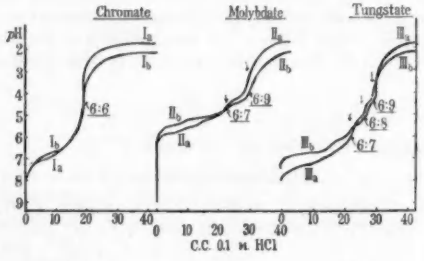

Fig. 4.—Potentiometric titration of sodium chromate, molybdate and tungstate with hydrochloric acid.

I a:	0.1 M Na_2CrO_4	I b:	0.02 M Na_2CrO_4
II a:	0.1 M Na_2MoO_4	II b:	0.02 M Na_2MoO_4
III a:	0.1 M Na_2WO_4	III b:	0.02 M Na_2WO_4

Data at different concentrations give exactly similar plots, and the displacements of the curves due to the dilution effects occur in each case. Curve Ia in figure 4a, curve IIa in figure 4b and curve IIIa in figure 4c indicate the titration curves of 0.1 M chromate, molybdate and tungstate with 0.1 M hydrochloric acid, while curve Ib, and curve IIb and curve IIIb in each figure indicate the titrations of 0.02 M of those salts with 0.1 M hydrochloric acid, respectively. Curves obtained for the higher concentration are steeper than those for the lower one. In figure 4b and 4c, two steep inflections occur in each curve at a XO_4^{--} to H^+ mol-ratios, 6:7 and 6:9, which have been attributed to the formation of the so-called para-molybdate and meta-molybdate ions, i. e., $HMo_6O_{21}^{5-}$ and $H_3Mo_6O_{21}^{3-}$, respectively, by Jander[4] and other authors[11][12]. The corresponding poly-anions of tungstate, para- and meta-tungstates, were observed prominently in the present investigation, though the *p*H ranges at which they are formed are different from those of molybdates. A steady inflection is revealed both in the titration curves of molybdate and tungstate, but it is not sufficiently pronounced. It is probably attributed to the existence of the poly-anion having the molar ratio, 6:4, that is, the formation of trimolybdate, $Mo_3O_{11}^{4-}$ as well as that of tritungstate, $W_3O_{11}^{4-}$, as suggested by Jander[4], but it could not be decided conclusively in this paper. Another steeper inflection at the mol-ratio, 6:8 occurs in titration curves of tungstate, IIIa and IIIb in figure 4c. It may be attributed to the existence of $H_2W_6O_{21}^{4-}$, but it is also not so pronounced as in the cases of para- and meta-tungstates. It has not been reported previously.

The equilibria between these poly-anions of tungstate, by analogy with those of molybdate may be formulated as follows:

(1) $6WO_4^{--}+4H^+=2W_3O_{11}^{4-}+2H_2O$

(2) $2W_3O_{11}^{4-}+3H^+=HW_6O_{21}^{5-}+H_2O$

or $6WO_4^{--}+7H^+=HW_6O_{21}^{5-}+3H_2O$

(3) $2HW_6O_{21}^{5-}+2H^+=2H_2W_6O_{21}^{4-}$

or $6WO_4^{--}+8H^+=H_2W_6O_{21}^{4-}+3H_2O$

(4) $HW_6O_{21}^{5-}+2H^+=H_2W_4O_{21}^{3-}$

or $6WO_4^{--}+9H^+=H_3W_6O_{21}^{3-}+3H_2O$

The mol-ratio and the *p*H ranges at which these poly-anions are formed are summarized in Table 4. Regarding to the titration curve of

Table 4

Mol-ratios and the *p*H Ranges of Poly-anions in Dilute Solutions

*p*H range	Mol-ratio Na_2MoO_4:HCl	Poly-anion
5.2	6 : 4	$Mo_3O_{11}^{4-}$
4.3—4.8	6 : 7	$HMo_6O_{21}^{5-}$
—	—	—
3.4—4.2	6 : 9	$H_3Mo_6O_{21}^{3-}$
*p*H range	Mol-ratio Na_2WO_4:HCl	Poly-anion
6.5	6 : 4	$W_3O_{11}^{4-}$
5.3—5.9	6 : 7	$HW_6O_{21}^{5-}$
4.5—4.9	6 : 8	$H_2W_6O_{21}^{4-}$
3.5—4.3	6 : 9	$H_3W_6O_{21}^{3-}$

(11) P. Souchay, *Ann. Chim.* **18** 61, 73, 169 (1934).
(12) G. Biehler, *Ann. Chim.* (12) **2**, 189 (1947).

chromate, no inflection but that at the mol-ratio, 1:1 could be found. It is attributable to the formation of bichromate ion, $HCrO_4^-$, as has been known. The further investigation on the electrolytic behaviors and the constitution of these poly-anions will be reported in the subsequent papers of this series.

Summary

(1) A vacuum tube potentiometer constructed in our laboratory has been used for the *p*H measurements with a glass electrode.

(2) A mathematical expression for the hydrolytic process has been given as a linear relation between the *p*H values and concentrations of the solutions.

(3) Hydrolyses of chromates, molybdates and tungstates in dilute solutions have been observed.

(4) The existence of dimolybdate and ditungstate ions, $Mo_2O_7^{--}$ and $W_2O_7^{--}$, as well as that of bichromate ion, $HCrO_4^-$, in dilute solutions were confirmed by measuring the *p*H values at varying dilutions.

(5) An empirical formula for expressing the relationships between the *p*H values and concentrations of the solutions was proposed for chromate, molybdate and tungstate solutions.

(6) The similarities of the electrolytic behaviors between tungstate and molybdate as well as the dissimilarities of those between chromate and molybdate or between chromate and tungstate have been ascertained by means of potentiometric studies.

(7) It has been observed by these studies that the strength of the acids increases with the atomic weights of these acidic metals.

(8) The existence of para- and meta-poly-anions of tungstate as well as those of molybdate were confirmed by potentiometric titration of molybdate or tungstate with hydrochloric acid.

(9) A steady inflection at the mol-ratio, 6:4, is revealed both in molybdate and tungstate solutions, but it is not sufficiently pronounced. Another break at the mol-ratio, 6:8, was found in the titration curve of tungstate solution.

(10) No break but that at the mol-ratio, 1:1, which is attributable to the formation of bichromate ion could be found in the titration curve of chromate. It gives further confirmation of the dissimilarity between chromate and molybdate as well as tungstate.

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Electrolytic Behavior of Elements of the Group VIa in the Periodic System. II. Conductometric Studies on the Chromate, Molybdate and Tungstate Ions

By Kuan PAN, Sui Fong LIN and Shong Tsuo SHENG

(Received april 11, 1952)

Since the initial development of the alternating-current conductivity bridge by Kohlrausch[1], various technical advances[2] have been made in the source, in the bridge, or in the cell design and detection of the alternating-current signal. Though a properly constructed telephone receiver[3] has been used, in general, as a suitable detector for determining the setting of the alternating-current bridge, the nervous strain of listening to very weak notes is still unavoidable, especially in the case of high resistance.

As a result of advances in the field of electronics, however, the electric eye[4] and the cathode-ray oscillograph[5] have been proposed for this purpose.

(1) F. Kohlrausch, *Z. physik. Chem.*, **2**, 561 (1888).

(2) G. Jones and R. C. Josephs, *J. Am. Chem. Soc.*, **50** 1049 (1928); P. H. Dike, *Rev. Sci. Instruments*, **2**, 379 (1931); T. Shedlovsky, *J. Am. Chem. Soc.*, **52**, 1793 (1930).

(3) E. W. Washburn and E. Parker, *J. Am. Chem. Soc.*, **39**, 238 (1917).

(4) Hovorka and Mendenhall, *J. Chem. Education*, **16**, 239 (1939).

(5) Lamson, *Rev. Sci. Instruments*, **9**, 272 (1938).

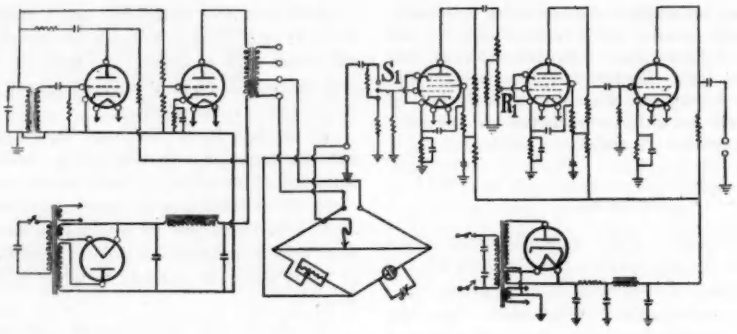

Fig. 1.

In the present investigation, measurements of the equivalent conductivities of chromate, molybdate and tungstate as well as conductometric titrations of these salts with hydrochloric acid have been carried out by using cathode-ray oscillograph as a detector for increasing the sensitiveness of the bridge setting and performing the rapid measurements.

Experimental

(1) **Materials.** — Conductivity water having a specific conductivity of 1.6 to 2.4×10^{-6} mho used in this experiment was purified by distillation according to the procedure described in the previous paper[6] of this series. The constant boiling fraction of hydrochloric acid was diluted to the desired concentration for use in the conductometric titrations.

All the salts used in the present investigation were purified by the repeated recrystallization from conductivity water as described in the previous paper[6]. After desiccating the salts in vacuo at room temperature, the crystalline water and the composition of the salts were checked by gravimetric analysis.

The solutions used for conductometric measurements were prepared, directly, by dissolving the salt in carbonate-free conductivity water and diluted to a desired concentration before each run.

(2) **Apparatus.** — Schematic diagrams of the apparatus used for the conductometric measurement in the present investigation are given in Fig. 1. A Shimazu KR-2 type Kohlrausch bridge (B), made in Japan, has been used for this purpose with 1000 cycle alternating-current supplied by an audio-frequency oscillator (A). The bridge output voltage is amplified by a three-stage variable amplifier (C), and then supplied to the vertical deflecting plate of a cathode-ray oscillograph. Dotted lines surrounding each unit of the set indicate the electrostatic shielding. Although a simple cathode-ray oscillograph was used previously by W. Juda and his co-workers[7] as a detector of the bridge setting, a Du Mont 208 type cathode-ray oscillograph has been successfully used in this experiment. When the circuit is in action, any wave pattern on the cathode-ray screen indicates the unbalanced bridge, while a single straight line indicates the balanced bridge.

An unbalance of about 0·1 ohm could be detected and the sensibility of detection could be controlled as desired by adjusting R_1 and S_1 in Fig. 1, the gain control of the cathode-ray oscillograph.

While a conductance cell of the modified Jones and Bollinger type[8] consisting of a glass vessel in which two platinum plates of 1.5 cm in diameter are fixed in parallel and platinized in ordinary manner, was used for the measurements of specific conductivity, two platinized platinum wires of 4 cm. in length and 1 mm. in diameter fused in a glass bead were used as the cell electrodes for the conductometric titration in order to attain a rapid equilibrium.

The conductance cell was immersed in a water thermostat whose temperature has been kept at 25 ± 0.05°C. for the specific conductivity measurements, and at 35 ± 0.05°C. for conductometric titration, since the room temperature was as high as 32—33°C.

Results and Discussion

(1) **Equivalent Conductivities of Sodium chromate, Molybdate and Tungstate.**—The equivalent conductivities of sodium chromate, molybdate and tungstate measured in this experiment at varying dilution are plotted against $\sqrt{10^3 C}$ or $\log V$, as shown in Fig. 2 and Fig. 3. Since the equivalent conductivities of these salts increase rapidly with the dilution, especially at extreme dilution, the limiting

(6) K. Pan and T. M. Hsu: This bulletin, **26**, 126 (1953).

(7) G. Jones, R. Myels and W. Juda, *J. Am. Chem. Soc.*, **62**, 2919 (1940).

(8) G. Jones and G. M. Bollinger, *J. Am. Chem. Soc.*, **53**, 411 (1931).

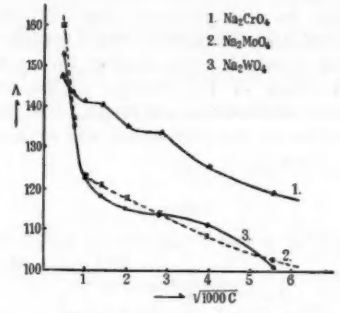

Fig. 2.—Λ and $\sqrt{1000 \times C}$.

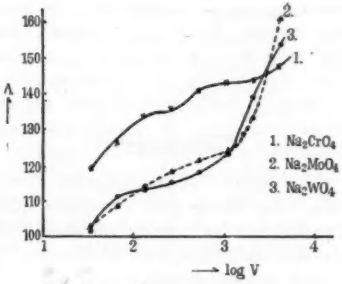

Fig. 3.—Λ and $\log V$.

value of equivalent conductivity of each salt at infinite dilution can not be estimated in the usual way. It may be attributable to the increasing degree of hydrolysis of these salts in dilute solutions and therefore, is probably due to the fact that, as the result of hydrolysis, the steady increase in the OH^- ion would lead to a rapid increase in conductivity of each salt solution, owing to the great equivalent ionic conductivity of the OH^- ion. These results are in good agreement with those obtained in the previous paper[6] which considered the hydrolytic process of molybdates and tungstates as follows:

$$2XO_4^{--}+H_2O=X_2O_7^{--}+2OH^-$$

In this case, as degree of hydrolysis increase with the dilutions, x mol. of XO_4^{--} ion will be replaced by $x/2$ mol. of $X_2O_7^{--}$ and x mol. of OH^- ion which would lead to a rapid increase in conductivity.

Throughout the entire experimental concentration range, the equivalent conductivity of chromate is greater than those of molybdate or tungstate. It may be attributable to the different type of hydrolysis, as shown in the previous paper[6], for the chromate ion,

$$CrO_4^{--}+H_2O=HCrO_4^-+OH^-$$

The similarity between the former, i. e. molybdate and tungstate as well as the dissimilarity between the latter, i. e. chromate and molybdate or tungstate, is confirmed also in this experiment.

Table 1

Equivalent Conductivities of Sodium Chromate, Molybdate and Tungstate at Varying Dilutions at 25°C.

Dilution, V (l./equiv.)	$\log V$	$\sqrt{10^3 C}$	Equivalent Conductivities		
			Na_2CrO_4	Na_2MoO_4	Na_2WO_4
32	1.51	5.59	119.3	102.5	101.0
64	1.81	3.95	125.6	108.4	111.1
128	2.11	2.80	133.9	113.8	113.5
256	2.41	1.98	135.4	117.9	115.2
512	2.71	1.39	140.6	121.3	117.9
1024	3.01	0.99	142.1	123.5	123.0
2048	3.31	0.70	143.2	135.5	138.9
4096	3.61	0.49	147.8	160.5	153.2
	$\Lambda_{1024}-\Lambda_{32}$		23	21	22

The differences between Λ_{1024} and Λ_{32}, $\Lambda_{1024}-\Lambda_{32}$, for sodium chromate, molybdate and tungstate solutions are found to be 23, 21 and 22, respectively, approximately equal to 2×10. The Ostwald's rule concerning the basicity and the difference, $\Lambda_{1024}-\Lambda_{32}$, for solutions of sodium salts seems to be held also in this case, though it has been mentioned that the sodium salts of the majority of inorganic acids do not follow this rule, in general. If it is not due to the accidental coincidence, it may be taken as due to the fact that molybdic or tungstic acid, or even chromic acid is a kind of weak dibasic acid similar to the weak dibasic organic acids. It is in accordance with the fact that molybdic and tungstic acids have their mean dissociation constants of the order of 10^{-5} as reported by Bhagwat and Dhar[9].

(2) **Conductometric Titration.**—Titration curves of 0.1 M and 0.02 M sodium chromate, sodium molybdate and sodium tungstate with 0.1 M HCl are shown in Fig. 4 and Fig. 5, respectively. Although one sharp break at the mol-ratio of 1:1, corresponding to the formation of bichromate ion is found in the titration curve of chromate, several kinds of breaks are found in the titration curves of molybdate and tungstate. Besides two sharp breaks at the points of XO_4^{--} to H^+ mol-ratios, 6:7 and 6:9, which have been taken

(9) W. V. Bhagwat and N. R. Dhar, *J. Indian Chem. Soc.*, **5**, 807 (1929).

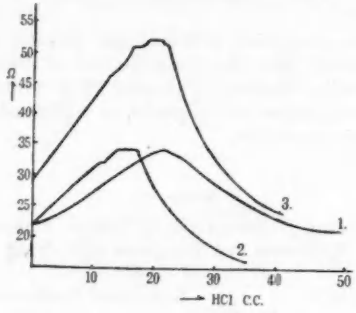

Fig. 4.—Conductometric titration of 0.1 M chromate, molybdate and tungstate with 0.1 M HCl.
1. 0.14 M Na_2CrO_4 15 cc.
2. 0.1 M Na_2MoO_4 15 cc.
3. 0.1 M Na_2WO_4 15 cc.

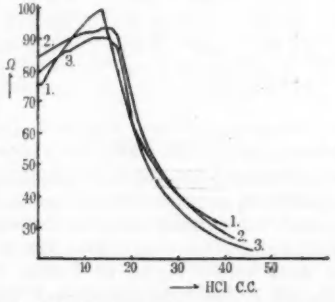

Fig. 5.—Conductometric titration of 0.02 M chromate, molybdate and tungstate with 0.1 M HCl.
1. 0.02 M Na_2CrO_4 75 cc.
2. 0.02 M Na_2MoO_4 75 cc.
3. 0.02 M Na_2WO_4 75 cc.

as the existence of para- and meta-poly-anions[10] were observed both in molybdate and tungstate, a remarkable break at the mol-ratio, 6:8, was observed in the case of tungstate. It is in good accordance with the result obtained in the previous paper[6]. Another break at 6:5.5, or 12:11, was observed prominently in the titration curves of molybdate but fairly in those of tungstate. It seems to be possibly attributable to the mixture of $[W_3O_{11}]^{4-}$ and $[HW_6O_{21}]^{5-}$, or to the formation of another kind of poly-anion.

When the sodium tungstate is allowed to stand over night before using for titration, however, a steady inflection is found at the mol-ratio, 6:4, which may be attributed to the formation of trimolybdate or tungstate as described in the previous paper[6], but we would not assert it until further confirmation could be obtained. The mol-ratios at which various kinds of recognizable breaks are revealed on the titration curves and the possible composition of the poly-anions are summerized in the Table 2.

Table 2

The Mol-ratios and Compositions of Poly-anions

Mol-ratio (calc.) $XO_4^{--}:H^+$	Poly-anion	Mol-ratio (obs.) $XO_4^{--}:H^+$		
		Na_2CrO_4	Na_2MoO_4	Na_2WO_4
6:4	$[X_3O_{11}]^{4-}$	—	6:4	6:4
6:5.5	$[HX_{12}O_{43}]^{13-}$?	—	6:5.5	6:5.5
6:6	$[HXO_4]^-$	1:1	—	—
6:7	$[HX_6O_{21}]^{5-}$	—	6:7	6:7
6:8	$[H_2X_6O_{21}]^{4-}$	—	—	6:8
6:9	$[H_3X_6O_{21}]^{3-}$	—	6:9.1	6:9

Summary

(1) Conductance measurements of sodium chromate, molybdate and tungstate solutions were carried out by using a Du Mont 208 type cathode-ray oscillograph as a detector of the Kohlrausch bridge setting.

(2) Equivalent conductivities of chromate, molybdate and tungstate at varying dilutions were measured at 25°C., but the limiting value of the equivalent conductivity of each salt at infinite dilution could not be estimated by the usual way, owing to the hydrolysis of these salts.

(3) The similarity between molybdate and tungstate as well as the dissimilarity between chromate and each of the two others were confirmed also in the present investigation.

(4) The difference $\Lambda_{1024}-\Lambda_{32}$ was found to be approximately equal to 2×10 for these sodium salts. It seems to indicate that either molybdic or tungstic or even chromic acid may be a kind of weak dibasic acid if Ostwald's rule is applicable.

(5) Besides two breaks at the XO_4^{--} to H^+ mol-ratios, 6:7 and 6:9 were found in the conductometric titration curves of molybdate and tungstate, a new sharp break at the mol-ratio 12:11 was observed prominently in the titration curves of molybdate but fairly in those of tungstate.

(6) A break at the mol-ratio, 6:8, which was reported in the previous paper, was found also in the titration curves of tungstate.

Laboratory of Theoretical and Inorganic Chemistry, Science Department, National Taiwan University, Taipei, China

(10) G. Jander, K. F. Jahr and W. Heukeshoven, *Z. anorg. allgem. Chem.*, **187** 60, 129 (1930), **194**, 383 (1930).

The New Method of Polymerization of Vinyl Compounds. I.[1] On the Polymerization of Methyl Methacrylate with Copper or Cuprous Chloride and Acids at Room Temperature

By Ryozo INOUE and Takashi YAMAUCHI

(Received June 16, 1952)

Introduction

We have discovered some new methods of polymerization of vinyl compounds, which are entirely different from the previous methods catalyzed by peroxides. Our methods are peculiar because they are able to perform polymerization very rapidly in good yield at room temperature. In this report we have treated the polymerization of methyl methacrylate with copper or cuprous chloride and acids. Copper has hitherto been considered in contradiction to our experimental results, as an anticatalyst in polymerization. For example, it has been applied as an inhibitor in the case of synthesis of methacrylate.

Experimental

In the following experiments we have applied methacrylic methyl ester as a vinyl monomer. We have, however, used aqueous solution of the ester in order to simplify experiments. As the solubility of this ester is only about 1% at room temperature, the polymerization in a considerably dilute solution is to be discussed in this report.

As an orientation, the accelerating power of the combination of the powder of metallic copper and various acids for polymerization are shown in Table 1.

The rate of polymerization, after about 1 weight % of the powder of metallic copper is thrown into the aqueous solution which contains 1% of methyl methacrylate and acid respectively is shown in the above Table. The reaction vessel was agitated vigorously at first and then allowed to stand. Generally speaking, the lower the molecular weight of organic acid is, the stronger the accelerating power for polymerization becomes, and in this case inorganic acids are not so useful. But as it will be shown later, this tendency as for the accelerating power is of course different when other kinds of metal or its lower valencial salts are used. What is important is that the polymerization is accelerated by the preceding system.

The course of the polymerization with the powder of metallic copper and formic acid is shown in Fig. 1.

(1) This paper was read in the annual meeting of the Chemical Society of Japan in April, 1952.

Table 1

The Accelerating Power of the System of the Powder of Metallic Copper and Various Acids for the Polymerization of the Methyl Methacrylate (at Room Temperature)

Formic acid	##	Lactic acid	+
Acetic acid	##	Benzoic acid	+
Propionic acid	#	Sulfuric acid	#
Butyric acid	+	Hydrochloric acid	#
Isovalerianic acid	+	Phosphoric acid	#
Oxalic acid	##		

where

means that the white precipitate (polymer) is produced within five minutes after the powder of metallic copper is thrown into the solution.

means that the white precipitate (polymer) is produced within thirty minutes after the powder of metallic copper is thrown into the solution.

\+ means that the white precipitate (polymer) is produced within several hours after the powder of metallic copper is thrown into the solution.

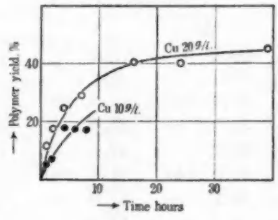

Fig. 1.

In the figure we have shown two examples with a different ammount of copper powder, i. e. 20 g./l. and 10 g./l. The solution contained 0.096 mol./l. methyl methacrylate and 0.115 mol./l. formic acid. Though an ammount of the copper powder has influence on the velocity of the polymerization, it is not easy to find any quantitative relations. It is worth notice that though the powder of metallic copper precipitates to the bottom of the vessel as a result of quiscence throughout the polymerization, separation of

polymers can be observed all over the solution (system) and that the induction period is not to be observed.

If we apply Cu_2Cl_2 instead of metallic copper, more rapid and more uniform polymerization will happen, as Cu_2Cl_2 is somewhat soluble in water. We have shown the influence of the amount of Cu_2Cl_2 and the concentration of formic acid on polymerization in Tables 2 and 3. In these experiments we have stirred the solution slowly.

Table 2

The temperature of polymerization: 40°C.
Methyl methacrylate :0.096 mol./l.
Formic acid :0.201 mol./l.

Time of polymerization (hours)	Amount of Cu_2Cl_2 (g./l.) 15 Yield (%)	$\bar{P}$	10 Yield (%)	$\bar{P}$	5 Yield (%)	$\bar{P}$
0.5	19.2	170	27.5	140	35.6	100
1.0	39.6	—	39.9	—	29.0	—
1.5	43.1	—	52.3	—	50.9	—
2.0	50.5	160	(36.7)	150	56.7	140
3.0	51.3	—	60.4	—	60.2	—
4.0	59.0	—	62.9	—	61.1	—
5.0	60.6	—	60.2	—	61.7	—
6.0	60.9	—	62.5	—		
7.0	62.7	—			64.0	—
8.0	60.9	140	55.5	140	62.9	130
24.0	62.7	140	(85.4)	130	69.6	120

Table 3

The temperature of polymerization: 40°C.
Methyl methacrylate :0.096 mol./l.
Formic acid :0.392 mol./l.

Time of polymerization (hours)	Amount of Cu_2Cl_2 (g./l.) 5 Yield (%)	$\bar{P}$	1 Yield (%)	$\bar{P}$	0.5 Yield (%)	$\bar{P}$
0.5	21.3	120	19.2	180	27.1	350
1.0	36.5	—	35.0	—	37.9	—
1.5	43.4	—	42.5	—	47.9	—
2.0	49.2	140	51.6	260	45.4	360
3.0	53.1	—	51.0	—	45.0	—
4.0	56.5	—	51.0	—		
5.0	58.8	—	50.8	—	44.7	—
6.0	58.8	—	49.8	—	44.0	—
7.0	62.3	—	49.1	—	44.6	370
8.0	54.8	140	49.0	240		
24.0	61.0	130	51.6	250	46.9	370

Though the concentration of the formic acid does not suffer a change such as can be detected by ordinary titration, the reaction mixture becomes green with the lapse of time. The polymerization stops in about two hours presumably in consequence of the exhaustion of Cu_2Cl_2; it proceeds again as shown in Fig. 2 when Cu_2Cl_2 is added anew (arrow in the Fig.).

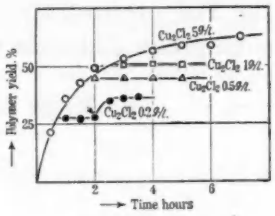

Fig. 2.

Discussion

In the reaction of the above experiments, free radical of hydrogen is produced, which can initiate the chain polymerization.

$$Cu + RCOOH \rightarrow Cu^+ + RCOO^- + H\cdot$$
$$Cu^+ + RCOOH \rightarrow Cu^{++} + RCOO^- + H\cdot$$

As H· is very unstable or reactive in comparison with benzoate radical, if the concentration of H· is somewhat high, the initiation and stabilization reaction happen at once and in an extreme case merely hydrogenation may be observed. The conditions of the above experiments allow a primary free radical to have enough time to repeat chain propagation about two hundred times before it stabilizes as the result of collision with another free radical. In other words the concentration of H· is very low in comparison with an ordinary polymerization, the catalyst of which is benzoyl peroxide. It is known that Cu or Cu_2Cl_2 is stable to acids (for example CH_3COOH and HCOOH). Therefore we may find more general combinations of acids and metals or their lower valencial salts. These kinds of metals or salts have hitherto been generally known as anti-catalysts of polymerization. The polymerization of methyl methacrylate by hydrazine and platinum[2], or formic acid and palladium[3], were reported by Paravano as experimental researches. According to the results of the present experiments, the degree of polymerization is not yet so high, but we think that this new method of polymerization is interesting both from scientific and technical points of view.

Summary

(1) It has been that the polymerization of

(2) G. Paravano, *J. Am. Chem. Soc.*, **72**, 3855 (1950).
(3) G. Paravano, ibid., **72**, 5546 (1950).

methyl methacrylate happens catalytically with Cu or Cu_2Cl_2 and acids at room temperature. Polymerization products were obtained as fine powder easily separable from the reaction mixture.

(2) It has been pointed out that the polymerization is initiated by free radicals of hydrogen.

(3) Calculating from the degree of polymerization of the produced polymers and consumed Cu_2Cl_2, the efficiency of the produced H· for the polymerization is not so good.

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The Catalytic Action of Organic Peroxides on the Polymerization of Ethenoid Compounds. I. The Activity of Substituted Benzoyl Peroxides in the Polymerization of Styrene

By Matsuji TAKEBAYASHI and Tadao SHINGAKI

(Received June 26, 1952)

It is possible from a study of the catalyzed polymerization of vinyl compounds to obtain information on the activity of the radicals derived from peroxides initiating the polymerization. Cooper[1], studying the polymerization of styrene with various types of substituted benzoyl peroxide has observed that electron-attracting substituents give radicals of lower activity, while electron-repelling ones increase the activity of the radicals. However, the velocity of initiation of catalyzed polymerization is affected not only by the activity of radicals, but also by the amount of active radicals which are produced in a unit of time. Therefore the velocity of decomposition of peroxides also seems to be an important factor. Swain and his co-workers[2] have reported that electron-attracting substituents retard the reaction and electron-repelling groups accelerate in the unimolecular thermal decomposition of *m*- and *p*- substituted benzoyl peroxides, and that the data fit the Hammett equation closely. Blomquist and Buselli[3], however, have indicated that the homolytic cleavage of symmetrical benzoyl peroxides into free radicals may involve the interaction of two opposing dipoles.

The present study was initiated to see the relation between the amount and the activity of the radicals initiating the polymerization of styrene. For this purpose, symmetrical *m*- and *p*- substituted benzoyl peroxides were taken up as the catalyst.

As an empirical measure of the activities of peroxides, styrene (1/30 mol.) was polymerized with various types of substituted benzoyl peroxide (1/3000 mol.) at 60°C. for eighteen hours in the absence of air, and the effects of peroxides on the rate of polymerization have been measured. The results obtained are summarized in Table 1.

Table 1

Substituted benzoyl peroxide	Rate of polymerization (%)	K of substituted benzoic acid at 25°C. ($\times 10^{-5}$)
p, *p'*-Dimethoxy	99.8	3.2
m, *m'*-Dimethoxy	85.7	5
p, *p'*-Dimethyl	91.6	4.4
m, *m'*-Dimethyl	82.0	5.6
Unsubstituted	81.5	6.69
p, *p'*-Dichloro	71.9	9.3
m, *m'*-Dichloro	57.3	15.5
p, *p'*-Dicyano	28.3	23.5
m, *m'*-Dicyano	31.5	19.9
p, *p'*-Dinitro	10.1	39.6
m, *m'*-Dinitro	11.2	34.5
None	1.5	

This experiment shows that the activities of the substituted benzoyl peroxides on the rate of polymerization of styrene are inversely proportional to the square root of the dissociation constants K of the corresponding substituted benzoic acids, and that better linearity is found when using $\sqrt{K}$ than when using Hammett's constant σ as shown in Fig. 1.

(1) W. Cooper, *Nature*, **162**, 897 (1948).
(2) C. G. Swain, W. H. Stockmayer and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950).
(3) A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.*, **73**, 2983 (1951).

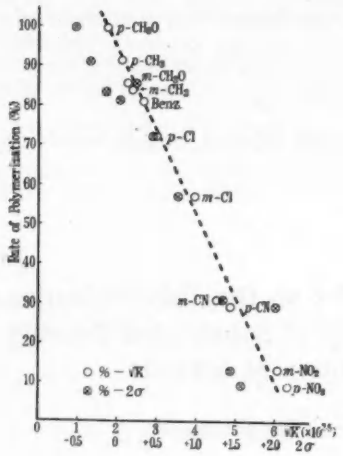

Fig. 1.

In order to elucidate the results described above, the authors observed, in the first place, the rate of decomposition of the peroxides in styrene at 60°C. for eighteen hours. The percentage of decomposition is plotted against $\sqrt{K}$ or 2σ in Fig. 2. This has been included as it shows that the rate of decomposition is inversely proportional to $\sqrt{K}$ and proportional to 2σ, and that better linearity is found with $\sqrt{K}$ than with 2σ.

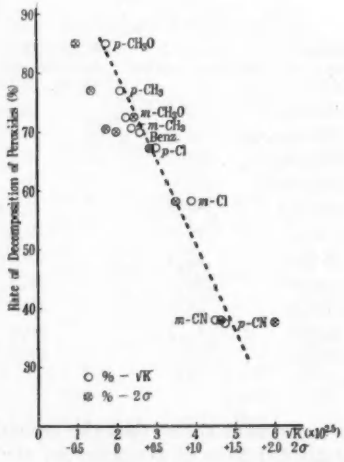

Fig. 2.

The next experimental problem was to determine the kinetic order of the thermal decomposition of the peroxides in styrene. The rate of decomposition of peroxides in solution is given generally by

$$-d[P]/dt = k_1[P] + k_i[P]^n,$$

where P expresses the concentration of the undecomposed peroxide, k_1 the rate constant of unimolecular decomposition, k_i that of induced decomposition, and n the kinetic order of induced decomposition.

The experiments with benzoyl peroxide and some substituted benzoyl peroxides (1 mol. % to styrene) were carried out at 60°C. The percentage of decomposition of peroxides was determined by the iodometric method according to the direction of Swain[2]. As for dinitrobenzoyl peroxides, the rate of decomposition was not measured exactly by this method because nitrobenzoic acids, produced during the reaction, had also an oxidizing action. The data are given in Fig. 3 and Table 2. The decomposition was observed to be of first order in all cases. Therefore, it should be possible to ignore the term for the bimolecular induced chain decomposition[4]. Then, we have

$$-d[P]/dt = k_1[P].$$

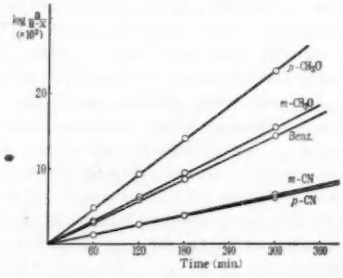

Fig. 3.

Table 2

Peroxide	$k_1\times10^4$, min.$^{-1}$	$\log(k/k_0)$
p,p'-Dimethoxy-benzoyl	17.7	0.206
m,m'-Dimethoxy-benzoyl	12.0	0.033
p,p'-Dimethyl-benzoyl	12.7	0.061
m,m'-Dimethyl-benzoyl	11.3	0.009
Benzoyl	11.05	0.000
p,p'-Dichloro-benzoyl	9.9	−0.047
m,m'-Dichloro-benzoyl	8.1	−0.135
p,p'-Dicyano-benzoyl	4.6	−0.380
m,m'-Dicyano-benzoyl	4.8	−0.362

Table 2 indicates also that the greater the electron-affinity of substituentsis, the more

(4) Swain has obtained a different result in the thermal decomposition of benzoyl peroxide in styrene. His rate curve for decomposition shows a marked autocatalysis, which he has supposed to be due to overheating.

rapidly the peroxides decompose in styrene. The relation between $\log(k/k_0)$ and the rate of polymerization is shown in Fig. 4, where k indicates the rate constant of substituted benzoyl peroxides, and k_0 that of unsubstituted ones. It is recognized that the rate of decomposition of peroxides is in a parallel relation with the rate of polymerization of styrene.

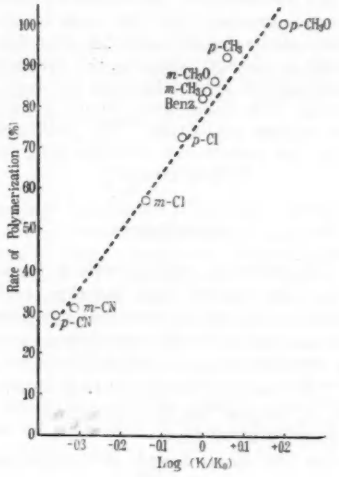

Fig. 4.

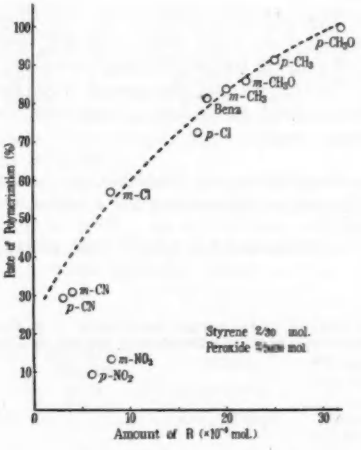

Fig. 5.

Considering that the thermal decomposition of peroxides in styrene is an unimolecular reaction, it is supposed that the radicals acting as the initiator of the polymerization are chiefly benzoate radical RCOO and aryl radical R, produced from the radical RCOO, and that the larger the amount of the radicals which are produced in unit time, the greater the rate of polymerization of styrene. The amounts of various types of the radical R were estimated from those of the carbon dioxide which was generated. Then, the above expectation seems to be satisfied about the radical, R, excepting the cases of dinitrobenzoyl peroxides, as shown in Fig. 5. Concerning this subject, furthermore, the kinetic studies on the formation of carbon dioxide are under way.

In respect to the small activity of dinitrobenzoyl peroxides, a consideration has been deduced. Assuming that the segments of the peroxides form nitrobenzene and nitrobenzoic acids during the polymerization, it might be expected that these nitro-compounds would react as inhibitors of the polymerization[5].

It is possibly owing to the inhibiting action of the nitro-compounds described above that the rate of polymerization with dinitrobenzoyl peroxides is quite small in spite of the comparatively large rate of decomposition[3].

Experimental

Materials.—The styrene employed was distilled with steam, dried over small amount of calcium chloride, and distilled under reduced pressure just before use. b. p. 63°C./55 mm. The absence of peroxides was ascertained by the test with ferrous ammonium sulfate and ammonium thiocyanate. All substituted peroxides were prepared by the reaction of a solution of an acid chloride in dry toluene with an excess of aqueous sodium peroxide according to the method of Price and Krebs[6] used for p,p'-dinitrobenzoyl peroxide. In general, the melting points or decomposition points were quite sharp after recrystallization

Table 3

Peroxide	M. p. (Dec.) (°C.)	Purity (%)
p,p'-Dimethoxy-benzoyl	128	98.5
m,m'-Dimethoxy-benzoyl	82	99.0
p,p'-Dimethyl-benzoyl	136	98.3
m,m'-Dimethyl-benzoyl	54	99.0
Benzoyl	106—107	98.2
p,p'-Dichloro-benzoyl	140	99.0
m,m'-Dichloro-benzoyl	123	98.4
p,p'-Dicyano-benzoyl	176	98.0
m,m'-Dicyano-benzoyl	163	96.7
p,p'-Dinitro-benzoyl	158	99.1
m,m'-Dinitro-benzoyl	137	98.0

(5) S. Okamura, K. Uno and K. Yamamoto, read at the fifth annual meeting of the Chemical Society of Japan, April 4, 1952; C. C. Price, "Mechanism of Reactions at Carbon-Carbon Double Bonds", New York, 1946, p. 87.

(6) C. C. Price and E. Krebs, "Organic Syntheses", **23**, 65 (1943).

from hydrocarbon solvents, and represented to a fair extent the purity of the peroxide. In Table 3 are listed the substituted benzoyl peroxides employed in this study.

Polymerization of Styrene.—The polymerization of styrene was carried out in sealed 17 cc. reaction tubes. The tubes were treated with warmed cleaning solution for several hours, left standing in a very dilute solution of sodium bisulfate for a short time, then rinsed with distilled water, and dried. A peroxide (1/3000 mol.) was mixed with 1/30 mol. of styrene in the reaction tube, the tube cooled in an ice-salt-bath, then evacuated and sealed off. The sealed tube was warmed to room temperature and then immersed in a 60±0.05°C. thermostat for eighteen hours, then removed and cooled in an ice-salt-bath. Unchanged styrene was driven off in a vacuum and the weight of polystyrene was measured. In another experiment, the reaction products were dissolved in benzene and the polymer produced was precipitated by adding methanol to the solution. The weight of polystyrene was almost equal to that of the case mentioned above.

Decomposition of Peroxides.—The apparatus is shown schematically in Fig. 6. A is the reaction tube of 22 mm. diameter and 35 cc. capacity, B the inlet tube of 7 mm. diameter for nitrogen, C the cooler with cold water, and D the soda-lime tube for the absorption of the carbon dioxide which is generated. B was connected with the source of purified nitrogen. During the reaction a soda-lime tube E was attached to D.

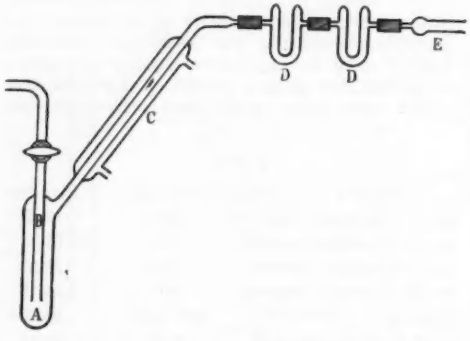

Fig. 6.

A mixture of peroxide (2/3000 mol.) and styrene (2/30 mol.) was taken in A and the tube A was cooled in an ice-salt-bath. Pure nitrogen[7] was passed through B into the whole apparatus. When the air in the apparatus was driven out, namely the weight of D had no longer increased, A was warmed to room temperature and then immersed in a 60−0.05°C. thermostat for eighteen hours. The reaction was carried out in a slow stream of nitrogen. After the required time, A was cooled, passing through nitrogen for one hour, and the weight of carbon dioxide absorbed in D was measured. In the experiments with peroxides such as benzoyl peroxide and dimethyl- and dichloro-benzoyl peroxide, the contents of A were dissolved in 30 cc. of benzene and hydrolyzed for twenty eight hours with 50 cc. of water and 4 g. of sodium hydroxide. The products were found to be chiefly the corresponding benzoic acids.

Summary

(1) The rates of polymerization of styrene with *m*- and *p*-substituted benzoyl peroxides have been found to be inversely proportional to the square root of the dissociation constants of the corresponding substituted benzoic acids.

(2) The thermal decomposition of the peroxides in styrene has been observed to be of first order in all cases.

(3) It has been found that the rate of decomposition of peroxides is in a parallel relation with the rate of polymerization of styrene.

(4) The relation between the amounts of radicals derived from the peroxides and the rates of polymerization has been studied.

(5) In respect to the small activity of dinitro-benzoyl peroxides, a tentative theory has been made.

The authors express their hearty thanks to the Ministry of Education for a grant.

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(7) Purified by the method described in L. F. Fieser, "Experiments in Organic Chemistry", 2nd Ed., New York, 1941, p. 395.

Cyclopolysiloxanes from Ethyldichlorosilane

By Rokuro ŌKAWARA, Eiji ASADA and Takeo WATASE

(Received July 24, 1952)

From the hydrolysis product of ethyldichlorosilane and from its pyrolysis product, cyclic polyethylpolysiloxanes of the general formula $(C_2H_5SiHO)_n$ were obtained analogous to those reported by Sauer[1] and Brewer[2] from methyldichlorosilane.

Experimental

Starting Materials. — The ethyldichlorosilane used in our experiments was prepared by the reaction of ethyl chloride with copper-silicon and was purified by fractionation through a 75 cm. helices packed column. The fraction having the boiling point 75.5°—76°C. (760 mm.) was taken as starting material. Analysis for hydrolyzable chlorine by hydrolysis in water-methanol solution and titration of the liberated acid indicated that our sample was pure ethyldichlorosilane[3]. *Anal.* Calcd. for $C_2H_6SiCl_2$:Cl, 54.96. Found: Cl, 54.5.

Hydrolysis.—To obtain the cyclic compounds ethyldichlorosilane has been hydrolyzed in ether solution according to Sauer's direction; e. g., two moles (258 g.) of ethyldichlorosilane was added to a mixture of 0.5 liter of diethyl ether and 1 kg. of cracked ice, which was vigorously stirred, over a half-hour period, some rubbery gel being produced. To avoid the gellation, ethyldichlorosilane was diluted with the same weight of diethyl ether and this solution was added to hydrolyzing mixture. Two typical experimental results are given in Table 1.

During the addition of ethyldichlorosilane, the temperature of the hydrolyzing mixture dropped from 0° to −8°C. As soon as the addition was completed the etherlayer was separated. Then the ice-cold water (the same weight as was used in the hydrolyzing mixture) was added and vigorous stirring was continued during an additional 15 minutes. The ether layer was washed repeatedly with water until it got neutral to methylorange and dried over dehydrated sodium sulphate.

Hydrolyzates

(a) **Untreated Hydrolyzate.** — The hydrolysis products were distilled by means of a Claisen flask containing a bundle of glass wool to prevent bumping. After ether was driven off at 760mm, the distillate was collected under 20 mm. The temperature of the oil bath was gradually raised to 220°C.

The temperature ranges and the amounts of distillate collected are given in Table I. Practically no distillate was given when the residue was further heated up to 240°C.

(b) **Thermally Rearranged Hydrolyzate.** — When the untreated hydrolyzate was distilled off, transparent sticky rubbery gel remained as the residue. By means of the pyrolysis of the residue under high vacuum using a rotary pump, the liquid distillate was acquired (Table 1) and there remained a small amount of transparent thin film stuck on the upper part of the flask. It may be seen from Table 1 that the ratio of untreated hydrolyzate to thermally rearranged hydrolyzate (Exp. 1, 11.2 g.: 21.3 g., Exp. 2, 40.7 g.: 34.8 g.) was greatly influenced by the hydrolyzing condition.

Cyclopolysiloxanes from (a) and (b). — The hydrolyzate (a) and (b) were rigorously fractionated through a 40 pair packed modified Stedman

Table 1

Exp. No.	$C_2H_5SiHCl_2$ diluted with (ether)	Hydrolyzing mixture		Hydrolyzate: Untreated — Distillate		Untreated — Still	Thermally rearranged — Distillate		Thermally rearranged — Still
		Ice	Ether	Temp. (20 mm.)	Yield	Temp.	Temp. (high vac.)	Yield	Temp.
	g.	g.	g.	°C.	g.	°C.	°C.	g.	°C.
1	100	500	200	100—130	11.2	—180	100—130	14.2	250—310
	(100)				0	180—220	130—170	7.1	310—400
2	250	1000	400	100—110	31.7	—140	100—140	19	250—310
	(250)			110—140	9	140—220	140—180	15.8	310—400

(1) Sauer, Scheiber and Brewer, *J. Am. Chem. Soc.*, **68**, 962 (1946).

(2) Brewer, *J. Am. Chem. Soc.*, **70**, 3962 (1948).

(3) Meals, *J. Am. Chem. Soc.*, **68**, 1880 (1946).

Table 2

Hydrolyzate	Fraction No.	n_D^{20} After days 1	3	8	60	d_4^{20} After days 1	3	60
Untreated	I (a)	—	1.4139	—	1.4139	0.9834	—	0.9838
	II (a)	—	1.4176	—	1.4176	0.9922	—	0.9918
Thermally rearranged	I (b)	1.4127	—	1.4138	1.4136	—	0.9820	0.9821
	II (b)	1.4179	—	1.4176	1.4175	—	0.9920	0.9922
	III (b)	1.4201	—	1.4201	1.4198	—	1.0025	1.0022

Table 3

	Mol. Formula	Mol. Wt. calcd.	Mol. Wt. found	Mol. Refn. calcd.	Mol. Refn. found	Si-H%(c) found	C %(d) found	H %(e) found	b. p. °C (20mm.Hg.)
I	$(C_2H_5SiHO)_3$	223	223	56.70(a)	56.63(b)	1.33	32.00	8.01	106
II	$(C_2H_5SiHO)_4$	297	294	75.60	75.39	1.28	32.63	8.07	135
III	$(C_2H_5SiHO)_5$	371	362	94.50	93.68	—	32.38	7.97	165

(a) Warrick: *J. Am. Chem. Soc.*, **68**, 2455 (1946).

(b) The values d_4^{20}: 0.9836, 0.9920, 1.0023; n_D^{20}: 1.4138, 1.4176, 1.4200 (cf. Table 2) are used for the calculation of I, II, and III respectively.

(c), (d), (e): Calculated values are 1.35, 32.43, and 8.16 respectively.

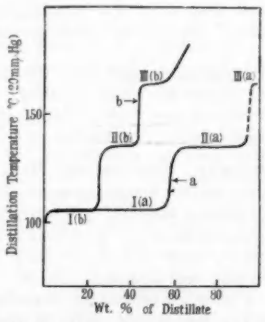

Fig. 1.—Distillation curve under 20 mm. Hg. (a) untreated hydrolyzate, (b) thermally rearranged hydrolyzate.

Distillation was performed in a course of about 7 hours.

Curve a: The fraction I(a) and II(a) were distilled out between the still-temperature of 140°—175°C. By stronger heating, between 270°—285°C the dotted curve was obtained.

Curve b: The fraction I(b) and II(b) were distilled out between the still-temperature of 170°—250°C, while III(b) was obtained between 250°—320°C.

column[4] respectively. The results are illustrated in Fig. 1.

Untreated hydrolyzate of several runs including Exp. 1 and 2 amounted to 68 g. By the rigorous fractionation, the two following fractions e. g. I(a) 40 g. and II(a) 19 g. were obtained and there remained some liquid and transparent gel. There must have occurred a partial thermal rearrangement of a lower boiling fraction to a transparent gel during a course of distillation. By stronger heating the fraction indicated by the dotted line was obtained but this fraction III(a) was not examined (Fig. 1).

Thermally rearranged hydrolyzate of several runs amounted to 97 g. By the rigorous fractionation, the three following fractions: I(b) 21 g., II(b) 14 g., and III(b) 7 g. were obtained. As shown in Fig. 1 (Curve b), above 165°C. no plateau was found. There remained some transparent rubbery gel in the still as was the case in the untreated hydrolyzate. It may be seen from these facts that a part of the lower boiling hydrolyzates polymerised to the gel.

Density and refractive index of these fractions are summarized in Table. 2.

From these data II(a) and II(b) may be regarded as the same compound. This conclusion was further supported by the molecular weight determination. The fraction I(b) which was assigned to cyclotriethyltrisiloxane by the molecular weight determination in dioxane, changed slightly its density and refractive index after a few days. But the marked changes such as Brewer[2] noted with the cyclotrimethyltrisiloxane were not found. As the molecular weight and other analytical data of this compound were the same as I(a), these may be regarded as the same compound.

The expected composition of these compounds was confirmed by determining the percentage hydrogen attached to silicon, % H(−Si), according to the equation

$$Si—H+KOH \rightarrow H_2+Si—OK$$

The samples (0.15—0.20 g.) were decomposed with 40% aqueous pottasium hydroxide solution in a Zerewitinoff apparatus. The results are given in Table 3.

Because of the identical elementary constitution of these compounds it was necessary to determine

(4) John and Rehberg, *Ind. Eng. Chem.*, **41**, 1038 (1949).

accurately their molecular weight in order to assign molecular formulas. Our determinations were made cryoscopically in dioxane with the results given in Fig. 2.

It may be seen from the figure that the association of cyclopolysiloxanes occurred in the solution. These observed values were extrapolated to zero concentration. The molecular weights thus obtained at zero concentration are listed in Table 3, together with the other analytical data.

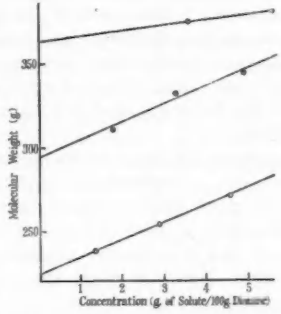

Fig. 2.—Cryoscopic molecular weight determanation in dioxane. Fisher's dioxane was distilled from sodium and the molar freezing depression constant $K=4.66$[5] was used.

(5) Landolt, Tabellen. Erg. II. b. 1468.

Since cyclic trimer was obtained in the untreated hydrolyzate, an enhanced reactivity of the siloxane linkage in these substances toward acid cleavage was not so distinct as Brewer indicated in the cyclopolymethylpolysiloxanes. This conclusion was further strengthened by the discovery that $(C_2H_5SiHO)_4$ is not readily converted in a short time into a high polymer by 20% aqueous hydrochloric acid as was the case with methyl analogue.

Summary

1. From the untreated hydrolyzate of ethyldichlorosilane, cyclic trimer $(C_2H_5SiHO)_3$ and tetramer $(C_2H_5SiHO)_4$, and from the pyrolyzed hydrolyzate cyclic trimer, tetramer and pentamer $(C_2H_5SiHO)_5$ have been acquired and characterized.

2. The reactivity of the siloxane (Si—O—Si) linkage in the $(C_2H_5SiHO)_n$ compounds toward acid cleavage appears to be not so enhanced as that exhibited by the $(CH_3SiHO)_n$ compounds.

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Untersuchung über Lignin und Zellstoff. I. Eine neue Bestimmungsmethode von Ligninsulfosäure in Sulfitablauge durch Kolloidtitration

Von Ryoiti SENZYU

(Eingegangen am 22, Juni, 1952)

Einleitung

Was die Bestimmungsmethode der Ligninsulfosäure in Sulfitablauge betrifft, so sind bisher verschiedene Verfahren veröffentlicht. Alle bisherigen Methoden liegen ausnahmslos auf dem Grund, die Ligninsulfosäure mit geeignetem Fällungsmittel fällen zu lassen und danach den Niederschlag zu wägen oder den restlichen Gehalt vom Fällungsmittel nach geeigneter Methode zu bestimmen.

Die bisherigen Forscher verwendeten als Fällungsmittel die mannigfachen Amine wie β-Naphthylamin[1], Chinolin[2], Benzidin[3], Trypaflavin[4], Anilin[5], Fuchsin[6], Benzacridin[7], Dimethylaminodiphenylmethan[8], usw., aber in allen Fällen ist die mit diesem aromatischen Amin ausgefällte Ligninsulfosäure nicht die gesamte, sondern nur ein Teil davon und die Verbindung der Ligninsulfosäure mit dem aromatischen Amin weist nicht ein stöchiometrisches Verhältnis auf. Nämlich die

(1) P. Klason, *Ber.* **20**, 703 (1929).
(2) K. Freudenberg u. F. Sohns, *Ber.* **66**, 262 (1933).
(3) B. Rassow u. H. Kraft, *Papier Fabr.* **29**, 80 (1929).
(4) A. Noll, ibid. **36**, 41 (1938).
(5) C. Doree u. L. Hall, *J. Soc. Chem. Ind.*, **44** 270 T (1925).
(6) Hennig, *Papier Fabr.* **30**, 179 (1932).
(7) W. Lautsch & G. Piazolo, *Cellulosechem.*, **22**, 48 (1944).
(8) H. Erdtmann, *Svensk Paperstidn*, **45**, 374-80 (1942).

Menge des Niederschlags der Ligninsulfosäure ist von derselben des hinzugesetzten Amins abhängig.

Die Bestimmungsmethode, die man heutzutage verhältnissmäsig öfter gebraucht, ist diejenige nach Partansky[9], wobei man als Fällungsmittel β-Naphthylamin benutzt. Die Menge der dabei ausgefällten Ligninsulfosäure ist aber nur 80 Prozent von gesamter Ligninsulfosäure in Ablauge. Um die Menge der Gesamtligninsulfosäure zu erhalten, muss man deshalb dem Gewicht des erhaltenen Niederschlags einen Faktor multiplizieren, der sich durch geringe Verschiedenheit der Versuchsbedingungen z. B. des Waschungsgrades des Niederschlags oder der Acidität der β-Naphthylaminlösung, verändert.

Als Bestimmungsmethode der Ligninsulfosäure in Sulfitablauge ist die Partanskysche Methode deshalb wenig geeignet. In Hinsicht auf die Analyse verschiedene Bestandteile in Sulfitablauge sind bisher verschiedene Methoden vorgeschlagt worden, aber keine geeignete quantitative Bestimmungsmethode der Ligninsulfosäure ist veröffentlicht. Dass die Kontrolle des Sulfitkochprozesses heute nicht auf der wissenschaftlichen Basis stehen kann, kommt wahrscheinlich aus Mangel an der schnellen und genauen Bestimmungsmethode der Ligninsulfosäure in Ablauge. Sowohl vom rein wissenschaftlichen Bedürfnisse als auch vom technischen müssen wir nun möglichst bald eine geeignete Bestimmungsmethode der Ligninsulfosäure in Ablauge feststellen. Hierbei müssen wir den Grund, der an den bisherigen Misserfolgen geknüft ist, eingehend untersuchen.

H. Terayama[10] hat in letzter Zeit als eine Bestimmungsmethode des hochpolymeren Elektrolyten die Kolloidtitration vorgeschlagt, derren Prinzip besteht darin, dass die gegenseitig anders geladenen Kolloidteilchen sich in stöchiometrischen Verhältnisse miteinander verbinden, um sehr schwerlösliche Produkte zu bilden. Diese Kolloidtitration ist im allgemeinen zur Bestimmungsmethode der hochpolymeren Elektrolyten verwendbar. Er bediente als ein positives Kolloid das Chitosan von Polymerizationsgrad etwa 20, das durch Alkalischmelz des Chitins hergestellt wurde.

Da auch die Ligninsulfosäure in Ablauge ein negatives Kolloid ist, so muss sie sich mit positivem Kolloidteilchen fällen. Je grösser dabei das Molekulargewicht des Fällungsmittel ist, um so vollkommener ist die Fällung der Ligninsulfosäure.

Wie bereits bekannt ist, ist in Ablauge ausser hochmolekularer Ligninsulfosäure noch eine ziemliche Menge niedermolekularer Ligninsulfosäure vorhanden. Um die Ligninsulfosäure in Anlauge quantitativ fällen zu lassen, muss man deshalb möglichst hochpolymere Amin bedienen. Nach meiner Versuche ist das Terayamaschen Chitosan als Reagens für Kolloidtitration nicht die geeignet. Nach meiner Meinung beruhe dies auf seine schwache schutzkolloide Wirkung und auf seine Niedermolekularität.

Die bisherigen Forscher haben sich vergebens anstrengt, von verschiedenen aromatischen Aminen ein gutes Fällungsmittel zu entdecken. Dieser Misserfolg kommt daher, dass die bisher geprüften Amine ausnahmslos niedermolekulare Verbindungen sind. Solange man daher als Fällungsmittel für Ligninsulfosäure das niedermolekulare Amin wie aromatisches Amin wählt, wird es wie man auch sich bemüht, nicht gelingen, ein geeignetes Fällungsmittel zu entdecken.

Von diesem Gesichtpunkte aus wählte ich als Fällungsmittel ein hochpolymeres Amin Oxyäthyl-Chitosan, dessen Polymerizationsgrad etwa 600 war, und es ist mir gelungen, die Ligninsulfosaure in Ablauge bis auf β-Ligninsulfosäure quantitativ fällen zu lassen und sie schnell und genau zu bestimmen. Bei bisherigen Methoden ist die restliche Menge des aromatischen Amins, mit Ausnahme der Methode nach Noll [7], nicht schnell bestimmbar, so dass man im einzelnen das Niederschlag wägen muss. Bei Kolloidtitration ist jedoch das unverbrauchte Glykol-Chitosan (abgekürtzt G. Ch.) mit kalium Polyvinylalkohol Sulfat (abgekürtzt P. V. S.-K) titrimetrisch bestimmbar. Wenn man vorher die Menge der Ligninsulfosäure, die sich mit ein Mol. G. Ch. (auf Aminogruppe berechnet) verbindet, nämlich das Äquivalentgewicht der Ligninsulfosäure gegen Aminogruppe weiss, so kann man gleich aus Verbrauch an G. Ch. den Ligninsulfosäuregehalt in Ablauge rechnen.

Versuchsteil

a) Herstellung des Glykol-Chitosan.— Zur Herstellung des G. Ch. wurde zuerst nach Senzyu und Okimasu[11] das Chitin glykoliert und dann wurde seine Acetylgruppe entfernt. 10 g. von dem nach Rigby[12] gewonnenen, fein

(9) A. M. Partansky u. Benson, Paper Trad J. **64, 102**, No. 7, 29 (1936).
(10) Terayama, *J. Polymer Science*, **8**, 243 (1952), "Chemical Research" **1**, (1949), **4**, (1953), (in Japanisch).
(11) R. Senzyu u. S. Okimasu, *J. Agri. Chem. Soc. Japan*, **23**, 437 (1949) (in Japanisch).
(12) Rigby, U. S. Patents 2,040,879 (1939).

gepulverten Chitin wurde durch 42%ige. Natronlauge 2 Stunden lang bei Zimmertemperatur behandelt und bis auf das vierfache Gewicht abgepresst. Das so erhaltene Alkalichitin wurde nach Thor und Henderson[13] in Kolben von 300 ccm. Inhalt mit 2.5 fachen Gewicht zerkleinertem Eis unter äuserer Kühlung gemischt, um Alkalichitin fein klar zu dispergieren.

Nachdem die Alkalikonzentration der viskosen Lösung mit 42%iger Natronlauge zu etwa 12 Prozent kontrolliert wurde, wurde 10 g. flüssiges Äthylenoxyd gegossen und gut geknetet. Der Kolben wurde mit Gummistopfel geschlossen, mit fliesendem Wasser allmählig erwarmt und dann 2 Stunden lang bei 25—30° stehen lassen. Die viskosen Lösung des glykoliertes Chitins wurde zunächst 12 Stunden lang bei etwa 60° erhitzt, um die Acetylgruppe zu entfernen. Das Produkt wurde mit dem Gemisch von Aceton und Alkohol abgeschieden. Zur Reinigung wurde mehrmals die Umfällung von wässeriger Lösung mit Alkolhol wiederholt. Der Polymerisationsgrad von dem erhaltenen G. Ch. nach Viskositätmesungen war etwa 600. Elementaranalyse;

	Gef. (%)	Ber. $(C_8H_{14}O_5NH_2)=206$ (%)
N-Gehalt (nach Kjeldahl)	6.71	6.82
NH_2-Gehalt (nach Vanslyk)	7.67	7.70

Die analytischen Date deuten darauf hin, dass das erhaltene Glykol-Chitosan dem Monoglykol-Chitosan entspricht, und dass die Entfernung der Acetylgruppe vollständig ist.

b) Herstellung des P. V. S.-K.—14 ccm Chlorsulfonsäure wurde trofenweise in dreihalsigem Rundkolben, in dem sich 60 ccm getrocknetes Pyridin befindet, unter kräftigem Rühren und kräftiger Kühlung hinzugefügt. Da der Inhalt später in weisse Masse erstarrt, so wurde der Kolben im Wasserbad erhitzt, um den Inhalt zu schmelzen. Nachdem 5 g. gut getrocknetes pulverförmiges Polyvinylalkohol allmählich hinzugegeben worden war, wurde der Kolben bei 100° 4 Stunden lang unter kräftigem Rühren erhitzt. Das dick flüssige Produkt wurde in 300 ccm. Wasser eingegossen und nach Zentrifugierung mit grosser Menge von 95% igem Alkohol versetzt, um das Pyridinsalz von Polyvinylalkoholschwefelsäure fällen zu lassen. Das Produkt wurde mit KOH in Kaliumsalz gespaltet. Zur Reinigung wurde die Umfällung mit Alkohol und Wasser wiederholt. Aus der Bestimmung des Schwefelgehalts vom Produkt ging es hervor, dass das Produkt 92.5% verestert war.

Ausführung der Bestimmung

Reagenzien.—Zum Titrieren dienen n/100-G. Ch.-und n/400-P. V. S. -K-lösung (auf NH_2-und Sulfogruppe berechnet). Löst man 0.4380 g P. V. S.-K (Schwefelgehalt 18.26%) in 1000 ccm Wasser, so erhalt man gleich n/400-P. V. S.-K-lösung. Zur Herstellung des n/100-G. Ch.-lösung löst man etwa 2.5 g. von lufttrockenen G. Ch. in 1000 ccm. Wasser, mit Essigsäure oder Salzsäure schwach säuert (pH 3-4), um die gesamte Aminogruppe in G. Ch. dissoziieren zu lassen. Die Konzentration der Aminogruppe der G. Ch.-lösung ist durch Titrieren mit n/400-P. V. S.-K bestimmbar. Beim Titrieren setzt man als Indikator einen Tropfen von 0.1 %iger Toluidinblaulösung zu. Solange der G. Gh. mindestens vorhanden ist, ist die Lösungsfarbe rein blau, aber sobald man die P. V. S.-K-lösung um einen Tropfen mehr als äquivalente Menge gegen G. Ch. hinzufügt, verändert sich seine Farbe rotviolet. Der Titrationsendpunkt ist innerhalb Fehlergrenz von 0.05 ccm genau bestimmbar.

Das nach Vanslyk bestimmte NH_2-Gehalt stimmt gut mit dem durch Kolloidtitration gefundenen überein. Dies deutet darauf hin, dass P. V. S.-K sich in dem klaren stöchiometrischen Verhältniss mit G. Ch. verbindet.

Methode.—Zum 5 ccm. der zwanzigfach verdünnten Ablauge setzt man je nach der Konzentration der Ligninsulfosäure 5-10 ccm. n/100-G. Ch.-lösung zu. Die Ligninsulfosäure fällt im Anfang flockig, aber danach wird ein Teil des Niederschlags wegen der starken schutzkolloiden Wirkung von überschussigem G. Ch. milchartig verteilt. Man verschliesst den Kolben mit Gummistopfen und schüttelt kräftig durch, um den Niederschlag der Ligninsulfosäure mit Luftblase an Oberflächen der Lösung zu bringen und damit bei Bestimmung des Endpunktes der Kolloidtitration zu erleichtern. Man gibt dann einige Tropfen von 0.1 %iger Toluidinblaulösung zu und titriert das überschussigen G. Ch., das sich mit der Ligninsulfosäure nicht verbindet, mit n/400-P. V. S.-K lösung zurück. Sobald die äquivalente Menge von P. V. S.-K hinzugefügt wird, wird die bisher trübende Lösung augenblicklich klar, und seine blaue Farbe verändert sich rotviolet und gleichzeitig sammelt sich der milchartig verteilte Niederschlag flockig an

(13) C. J. B. Thor und W. F. Henderson, *Amer. Dyestuff Reptr.*, **29**, 461 (1940).
(14) A. Nall, Papier Fabr. **36**, 43 (1938).

Oberflächen. Der Endpunkt dieser Kolloidtitration ist auch ohne Indikator innerhalb Fehlergrenz von einem Tropfen genau bestimmbar. Der Verfasser pflegt immer ohne Indikator auszuführen. Bei der Titration der sehr verdünnten Ablauge ist es aber vorteilhafter, Indikator zu benutzen. Aus der Differenz zwischen Blindversuch und Bestimmung kann man gleich den Polyaminverbrauch der Probeablauge ermitteln.

Der Polyaminverbrauch von Sulfitablauge ist unabhängig von der Menge des zugesetzten G. Ch., was bei volumetrischer Analyse sehr wichtig ist. Durch Elementaranalyse der Verbindung der Ligninsulfosäure mit G. Ch. ist der Verhältniss von Schwefel zu Stickstoff 1:1. Diese Tatsache deutet darauf hin, dass die Verbindung der Ligninsulfosäure mit G. Ch. sauberes stöchiometrisches Verhältniss aufweist. Man kann deshalb die Menge der aus einem Mol. NH_2-Gruppe entstehenden Verbindung, nämlich das Äquivalentgewicht der Ligninsulfosäure gegen NH_2-Gruppe rechnen, indem man vom Gewicht der Verbindung der Ligninsulfosäure mit G. Ch. das bekannte Äquivalentgewicht des G. Ch. ($C_8H_{14}O_5NH_2=206$) abzieht. Die Ziffern in Tabelle 1 Spalte 5 zeigen das Äquivalentgewicht der Ligninsulfosäure.

Trotzdem die Ablague von Tabelle 1 und 2 aus zwei anderen Zellstofffabriken geschenkt sind, hat ihre Ligninsulfosäure dasselbe Äquivalentgewicht (etwa 380), das von der Kochzeit unabhängig ist.

Um die Ligninsulfosäure in Ablauge zu bestimmen, braucht man nicht den Niederschlag der Kolloidtitration im einzelnen zu wägen, weil das Äquivalentgewicht der Ligninsulfosäure im allgemeinen konstant ist. Vom dem Polyaminverbrauch einer Sulfitablauge aus kann man gleich ihren Ligninsulfosäuregehalt rechnen, wobei 1 ccm. $n/400$-G. Ch.-lösung 0.95 mg. Ligninsulfosäure entspricht. Diese Methode ist besonders darin überlegen, dass die Bestimmung auf volumetrische Weise ausserordentlich schnell ausführbar ist und derren Genauigkeit sehr gross wie später erwähnt. Deshalb ist diese Kolloidtitrationsmethode als eine Kontrollmethode des Sulfitkochprozesses zu empfangen. Bisher litten Zellstofftechniker unter Mangel an schneller Bestimmungsmethode von Ligninsulfosäure. Jedoch können sie nun mit Hilfe des G. Ch. den Verlauf des Sulfitkochprozesses mit der Zeit erkennen.

Einfluss der *p*H-Wert bei Kolloidtitration auf Polyaminverbrauch

Da die Kolloidtitration an Bestimmung von

Tabbele 1

Die Ablauge von Papierzellstoff-Fabrik

Kochzeit in Min.	Ablauge cc.	Addierte cc. $n/100$-G. Ch.-Lös.	Verbrauchte P. V. S.-K zur Zurücktitr.		Verbrauchtes G. Ch. für Fällung		Niederschlag mg./cc. Ablauge	L. S.-Gehalt mg./cc. Ablauge	Äquivalentgewicht der L. S.
			cc. $n/400$	mg.	cc. $n/100$	mg.			
460	3	23.00	11.20	9.0	20.7	42.7	132.1	80.3	388
520	3	27.60	9.50	7.7	24.6	50.9	148.0	89.4	363
570	2	25.00	10.00	8.1	22.5	46.4	140.0	85.5	380
610	2	26.00	5.70	4.6	24.6	50.6	147.6	92.4	377
640	2	30.00	9.00	7.3	27.8	57.2	168.0	105.9	383
660	2	30.00	2.80	2.3	29.3	60.4	175.3	112.6	385

Tabbele 2

Die Ablauge von Kunstseidezellstoff-Fabrik

Kochzeit in Min.	Ablauge cc.	Addierte cc. $n/100$-G. Ch.-Lös.	Verbrauchte P. V. S.-K. zur Zurücktitr.		Verbrauchtes G. Ch. für Fällung		Niederschlag mg./cc. Ablauge	L. S.-Gehalt mg./cc. Ablauge	Äquivalentgewicht der L. S.
			cc. $n/400$	mg.	cc. $n/100$	mg.			
420	1	22.00	11.50	9.3	19.13	39.4	121.1	72.4	379
450	1	24.00	10.40	8.4	21.40	44.1	134.0	81.5	381
510	1	27.00	9.35	7.55	24.66	50.8	151.5	93.2	379
570	1	27.00	7.55	6.1	25.00	51.5	155.1	97.5	390
600	1	27.00	6.50	5.30	25.38	52.3	152.9	95.4	376
690	1	27.00	3.80	3.1	26.05	53.7	155.3	98.6	378

Tabelle 3

Empfindlichkeit der Glykol-Chitosan-Reaktion

Sulfitablauge	Zu je 0.1 ccm. 0.1% iges Reagens zugesetzt Tropfen	1 Tropfen enthält Gamma Ligninsulfosäure	Ausfall der Reaktion	
			Glykol-Chitosan	Trypaflavin
10 cc. : 1000	1	32	starke Fällung	mit blossem Auge nicht mehr, mit der Lupe noch wahrnehmbare Fällung
5 cc. : 1000	1	16	starke Fällung	nicht mehr wahrnehmbar
2.5 cc. : 1000	1	8	schwache Fällung	〃
1.25 cc. : 1000	1	4	mit blossem Auge noch nehmbare Fällung	〃

dissoziierbaren Gruppen geknüpft ist, so verändert sich der Polyaminverbrauch der Ligninsulfosäure mit *p*H-Wert bei Kolloidtitration, denn es sind einige phenolische OH-Gruppe ausser Sulfogruppe in Ligninsulfosäuremolekule. Bei verschiedenen *p*H-Werten führte ich deshalb die Kolloidtitration durch. In Fig. 1 ist die Abhängigkeit des Polyaminverbrauch vom *p*H-Wert bei Titration gezeigt.

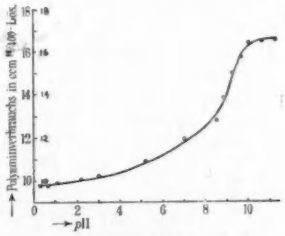

Fig. 1.—Die Abhängigkeit des Polyaminverbrauchs der Ligninsulfosäure in Sulfitablauge von *p*H-Wert bei Kolloidtitration.

Der Polyaminverbrauch nimmt plötzlich wöhrend von *p*H 8 bis 10 zu, aber bleibt ungefähr konstant unter *p*H 7. Dies deutet darauf hin, dass ausser Sulfogruppe und phenolische OH-Gruppe fast keine dissoziierbare Gruppe in Ligninsulfosäuremolekule seien. Wenn man die Titrierung im Bereich von *p*H 2-5 ausführt, so kann man die gute Reproduzierbarkeit erhalten. Der Verfasser pflegt immer in Gegenwart von etwas Essigsäure zu titrieren.

Unter *p*H 4 ist nur die Sulfogruppe und über *p*H 10 sind die gesamten dissozierbaren Gruppen titrierbar. Dass der Polyaminverbrauch bei *p*H 11 etwa 1.6 fach von demselben bei *p*H 3 ist, deutet darauf hin, dass die Ligninsufosäure in Sulfitablauge 2.8 Sulfpgruppen und 1.7 phenolische oder enolische OH-gruppen pro 840 g Lignin besitze.

Die Genauigkeit der Bestimmung

Da nach Noll[14] Trypaflavin sich von bisher aufgefundenen Fällungsmittel als das schärfste erwiesen hat, so wird es von Interese ist, die Empfindlichkeit der G. Ch.-Reaktion mit derselben der Trypaflavin-Reaktion zu vergleichen. Zu die sem Zweck wurde nach Noll je 0.03 ccm 0.15% iger G. Ch.-lösung mit je einem Tropfen extrem verdünnter Sulfitablauge versetzt. Die Ergebnisse sind aus der Tabelle 3 ersichtlich.

Noch bei einer Verdünnung von 1.25 : 1000 kann das G. Ch. die mit dem blossem Auge wahrnehmbare Fällung geben. Somit ist diese Raktion empfindlicher als die von Noll aufgefundene Fällungsreaktion mit Trypaflavin. Aus dieser Prüfung wird man ersehen, dass meine Bestimmungsmethode ausserordentlich genau ist.

Zum Schluss muss der Verfasser Herrn Prof. K. Nishida für seine freundliche Leitung sowie Herren M. Shimizu und I. Sakata, die mir arbeiten half, danken. Diese Untersuchung wurde mit Unterstützung der Takatiho Papierzellstoff-Fabrik geführt, wofür ich an dieser Stelle Dank sagen möchte.

Institut für Wissenschaft und Industrie,
Kyushu Universität

(14) A. Noll. Papier Febr., **36**, 43 (1938).

Untersuchungen über Lignin und Zellstoff. II. Eine neue Bestimmungsmethode des Lignins in Hölzern und Zellstoffen durch Kolloidtitration

Von Ryoiti SENZYU

(Eingegangen am 26, June, 1952)

Einteilung

Was die Bestimmungsmethode des Lignins in Hölzern und Zellstoffen betrifft, sind bisher verschiedene Methoden veröffentlicht, die man in zwei Gruppen d. h. die direkten und indirekten Methoden ordnen kann. Die direkten Methoden sind diejenigen, bei denen man die hochpolymeren Kohlenhydrate von Probe mittels starker Mineralsäure herauslöst und damit den Rückstand einfach als "Lignin" wägt.

Bei anderen bestimmt man mittelbar den Ligningehalt aus Methoxygehalt oder aus Verbrauch an Halogen oder Oxydationsmittel. Da jedoch die indirekten Methoden ohne Festlegung der genauen Versuchsbedingungen keine reichende Genauigkeit zu erwarten ist, so sind sie zur Bestimmung des Holzlignins heutzutage wenig gebraucht. Die heute häufigsten gebrauchten Methoden sind nämlich die direkten, bei denen man als Hydrolysemittel Schwefelsäure oder Salzsäure benutzt. Diese Methoden nahmen jedoch die zu längeren Ausführungsdauer in Anspruch. Es gibt leider noch keine Normalmethode für Ligninbestimmung.

H. Terayama[1] hat in letzter Zeit als eine neue Bestimmungsmethode der hochpolymeren Elektrolyten die Kalloidtitration vorgeschlagt. Der Verfasser[2] hat diese Kolloidtitration zur Bestimmung der Ligninsulfosäure in Sulfitablauge angewandt und die hinreichenden Resultate erhaltet, wobei er statt des Terayamaschen Chitosans das bei uns neurig hergestellten Polyamin d. h. "Oxyäthyl-Chitosan" Gebraucht, um die Endpunktbestimmung der Kolloidtitration leichter zu machen und bis auf die niedermolekularen Ligninsulfosäure quantitativ fällen zu lassen. Diese Kolloidtitration ist auch zur Bestimmung des Lignins in Hölzern und Zellstoffen ver wendbar.

Das Lignin eines verholzten Körpers verändert sich unter Einwirkung des Chlorgases in das Chlorlignin, das in verdünnten Alkali oder in 3% iger Natriumsulfitlösung leicht löslich ist. Auf diese Tatsache gründet sich die Cellulosebestimmung nach Cross und Bevan.[3]

In dem bei Gesamtcellulosebestimmung erhaltenen Waschabfall ist das gesamte Lignin der Probe als Chlorlignin (genauer gesprochen Chlorligninsulfosäure) gelöst. Wenn man das Chlorlignin in der Lösung bestimmen kann, so wird es gelingen, die Cellulose und das Lignin von Probe gleichzeitig zu ermitteln. Da die Chlorligninsulfosäure ein phenolische OH- und Sulfogruppe enthaltendes, negatives hochmolekulares Elektrolyt ist, so kann man sie mit Polyamin quantitativ fällen lassen. Indem man nach Zusatz einer bestimmter Menge der Polyaminlösung in die Lösung der Chlorligninsulfosäure das restliche Amin mit Kalium Polyvinylalkohol Sulfat zurücktriert, kann man gleich den Ligningehalt von Probe rechnen. Der Polyaminverbrauch der Chlorligninsulfosäure nimmt wegen ihrer phenolischen OH-gruppen mit dem PH-Wert bei Titration zu, um erst über *p*H 10.0 konstant zu werden. Deshalb muss man die Titrierung im Bereich über *p*H 10.0 ausführen, um immer die gute Reproduzierbarkeit zu erhalten. Aus diesem Grunde wählte ich als Fällungsmittel für Chlorligninsulfosäure N-polymethyl-Glykol-Chitosan (abgekürtzt M. G. Ch.), das noch im alkalischen Medium völlig dissoziierbar ist.

Versuchsteil

a) Herstellung des M. G. Ch.—4 g. Glykol-Chitosan wurde in 40 ccm. Wasser gelöst, mit 3.5 g. Natriumcarbonat, 15 g. Jodmethyl und 15 ccm. Methanol gut vermischt und in Druckflaschen bei 100° ein Stunde lang erhitzt. Das Produkt wurde mit Alkohol abgeschieden. Zur Reinigung wurde die Fällung von wässeriger Lösung mit Alkohol wiederholt.

(1) H. Terayama, *J. Polymer Science*, **8**, 243 (1952).
(2) R. Senzyu, *Bull. Chem. Soc. Japan*, **25**, 131 (1952).
(3) C. F. Gross and E. J. Bevan, *J. Chem. Soc. London*, **55**, 199 (1889).

Tabelle 1

1	2	3	4	5	6	7	8	9	10
Holzart	Ligningehalt nach 72% iger Schwefelsäure Methode, (%)	Menge des von 0.5 g. lufttrockener Probe extrahierten Lignins in cc. n/400 P. V. S.-K				Lignimmenge in 0.5 g. lufttrock. Probe, g.	Äquivalentgewicht des Lignins		
		erstmalige	zweitmalige	dritmalige	Gesamtsumme		Gefunden	Berechnet nach Annahme des Vorhandens von 6 Grup.	5 Grup.
"Akamatsu" Pinus densiflore	29.3	320	20	5	345	0.1270	147	140	168
"Masugi" Cryptomeria japonica	34.0	370	26	4	400	0.1476	147	140	168
"Buna" Fagus crenata Blume	25.9	230	14	2	246	0.1117	182	151	180
"Bambus"	26.0	220	18	2	240	0.1130	188	151	180

b) Ausführung der Bestimmung des Holzlignins

Reagenzien.—Zum Titrieren dienen n/100-M. G. Ch.-lösung und n/400-P. V. S.-K-lösung (auf Alkylamino- und Sulfogruppe berechnet).

Zur Herstellung der n/100 M. G. Ch.-lösung löst man etwa 3 g. lufttrockenen M. G. Ch. in 1000 ccm. Wasser und mit Ammoniakwasser alkalisiert. Durch Titrierung mit n/400-P. V. S.-K-lösung bestimmt man die genaue Konzentration der Alkylaminogruppe in Lösung.

Methode.—0.5 g. lufttrockenes Holzmehl, das man mit Wasser auffeuchtet, wurde in Glassfilter 15 Minuten lang Chlorgas einwirken lassen. Dabei kontroliert man die Geschwindigkeit der Durchführung von Chlorgas einige Blase pro Sekund. Nach Absaugen von haftenden Chlorgas wurde das chlorierte Holzmehl mit wenig Wasser einigemal gewaschen, um die bei Chlorierung gebildete Salzsäure zu beseitigen, und darauf 30 Minuten lang mit 10 ccm. 3% iger Natriumsulfitlösung auf Wasserbad erhitzt, womit das Chlorlignin sulfoniert wird und an Wasserlöslichkeit gewinnt. Das Holzmehl wurde dann mit heissem Wasser völlig gewaschen. Durch zweimalige Wechselwirkung von Chlorgas und Natriumsulfitlösung wurde das Lignin von Probe fast vollständig herausgelöst.

Das so erhaltene Filtrat wurde mit Ammoniak alkalisch gemacht und auf 100 ccm. aufgefüllt. Man gab in 10 ccm. davon 5 ccm. n/100-M. G. Ch.-lösung zu und titrierte das restliche Polyamin mit n/400-P. V. S.-K-lösung zurück. Bei Titrierung setzte man als Indikator einige Tropfen von 0.1% iger Toluidinblaulösung zu. Aus der Differenz zwischen Blindversuch und Bestimmung kann man den Polyaninverbrauch der Probelösung ermitteln.

Aquivalentgewicht des Lignins

Um aus dem polyaminverbrauch dieser Kolloidtitration den Ligningehalt der probe zu rechnen, muss die Polyaminverbrauch des anwesenden Lignins bekannt sein. Nimmt man an, dass die 72% ige Schwefelsäuremethode den echten Ligningehalt angebe, so kann man ein Äquivalentgewicht von Lignin gegen NH_2-gruppe erhalten. (siehe Tabelle 1 Spalte 5) Vorausgesetzt, dass der Grundmolekulargewicht des Nadel- und Laubholzlignins 840(nach Brauns[4]) und 910 (nach Harris[5]) sei, so kann man als ihre Aquivalentgewicht gegen Alkylaminogruppe die Ziffern in Tabelle 1 Spalte 9 und 10 erhalten.

Wie in Tabelle ersichtlich ist es höchst wahrscheinlich, dass die Chlorligninsulfosäure des Nadelholzlignins sechs dissoziierbaren Gruppen und diejenige des Laubholzlignins fünf besitze. Nach bisherigen Untersuchungen entsteht bei Chlorierung des Lignins grosse Menge der phenolischen OH-gruppen, die gegen gebund ene Chloratome äquivalent sind. Nach Fotijew[6] kann das Chlorlignin von Nadelholz wie folgt geschrieben werden.

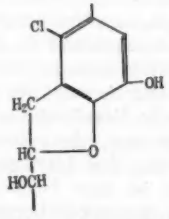

Fig. 1.—Schema des Chlorlignins.

Von dieser Tatsache aus ist es fast zweifellos, dass von sechs dissoziierbaren Guppen der Chlorligninsulfosäure des Nadelholzes fünf die phenolische OH-gruppe seien und eine die Sulfogruppe sei.

(4) F. E. Brauns, *J. Amer. Chem. Soc.*, **61**, 2120 (1939); *Paper Trad J.*, **108**, 42 (1939); ibid **111**, No. 14, 33 (1940).
(5) E. E. Harris, *Ind. Eng. Chem.*, **32**, 1049 (1940).
(6) S. A. Fotijew, *Pulp Paper Mag. Can.*, **39**, 749 1938) (C. Z. II. 218 (1939).

Einfluss der Versuchsbedingungen auf Ergebnisse

Der Polyaminverbrauch könnte mit der Einwirkungszeit und- Temperature des Chlorgases und mit der Erhitzungszeit in 3% iger Natriumsulfitlösung verändern. Ich untersuchte daher den Einfluss dieser Versuchsbedingungen auf Polyaminverbrauch des Lignins.

a) Einfluss von Temperatur. — 0.5 g. lufttrockenes Holzmehl wurde bei verschiedenem Temperatur chloriert, und die extrahierte Chlorligninsulfosäure wurde auf die ober erwähnte Weise bestimmt. Tabelle 2 zeigt die erhaltenen Ergebnisse.

Tabelle 2

Einfluss der Chlorierungstemperatur auf Polyaminverbrauch des Lignins
(Die Ziffern in Tabelle zeigen die Menge des extrahierten Lignins in ccm. n/400-P. V. S.-K-lös.)

Holzart	Temp., °C.		
	0	15	30
"Akamatsu" Pinus densiflora	350	352	347
"Sugi" Cryptomeria japonica	397	400	396
"Buna" Fagus crenata Blume	243	245	250
"Bambus"	240	238	240

Nach bisherigen Untersuchungen verändert sich das Chlorverbrauch des Holzes mit Temperatur. Wie aus Tabelle 2 ersichtlich ist jedoch das Polyaminverbrauch des Holzes von Einwirkungstemperatur des Chlorgases unabhängig. Aus dieser Tatsache geht hervor, dass die Menge der phenolischen OH-gruppe, die durch Einwirkung des Chlorgases in Ligninmolekül entsteht, von Temperatur unabhängig ist. Diese Einflusslosigkeit der Temperatur auf Polyaminverbrauch kommt wahrscheinlich auf vollkommene Chlorierung des Lignins. In diesem Punkte ist diese Methode den bisherigen Methoden überlegen, bei denen man aus Hologenverbrauch den Ligningehalt mittelbar bestimmt. Es ist sehr bemerkenswert, dass über 93% des gesamten Lignins durch nur einmalige Wechselwirkung von Chlorgas und Natriumsulfitlösung herausgelöst werden kann.

b) Einfluss der Einwirkungszeit des Chlorgases. — Wie ober erwähnt kann der grosste Teil des Lignins durch erstmalige Chlorierung und Extrahierung herausgelöst werden, deshalb kann man sagen, dass die Zeit der erstmaligen Chlorierung auf den Polyaminverbrauch entscheidend beeinflüsst. Aus diesem Grund prüfte der Verfasser nur den Einfluss der Zeit der erstmaligen Chlorierung. Das Chlorgas wurde stets bei 20° einwirken lassen. Die Ziffern in Tabelle 3 zeigen die Menge des erstmal extraheirten Lignins in ccm. n/400-P. V. S.-K-lösung.

Tabelle 3

Einfluss der Chlorierungsdauer auf den Polyaminverbrauch des Lignins

Holzart	Dauer in Min.			
	10	15	20	45
"Akamatsu" Pinus densiflora	320	345	349	345
"Buna" Fagus crenata Blume	231	246	248	247
"Bambus"	220	240	238	238

Wenn man über 15 minuten lang des Chlorgas durchgeführt, so kann man stets die guten reproduzierbaren Resultate erhalten. Es ist gleichgültig, ob die Dauer der zweitmaligen Chlorierung lang oder kurz sei. Diese Tatsache kommt wahrschienlich daher, dass meine Methode sich nicht auf die Bestimmung des Halogenverbrauch, sondern auf diejenige der phenolischen OH-gruppe gründet.

c) Einfluss der Erhitzungszeit mit Natriumsulfit.—Das Chlorlignin wurde unter Einwirkung des Natriumsulfites in die Chlorligninsulfosäure sulfoniert und gewinnt an Wasserlöslichkeit. So wird die Erhitzungszeit mit Natriumsulfit auf Sulfonierungsgrad des Lignins einflussreich sein. Die Tabelle 4 zeigt die erhaltenen Resultate.

Tabelle 4

Einfluss der Erhitzungsdauer mit Natriumsulfit auf den Polyaminverbrauch des Lignins

Extrahierungszeit in Min.	15	25	35	45
"Sugi" (Cryptomeria japonica	355	370	368	372

Die Ziffern in Tabelle zeigen die erstmal extrahierten Ligninmenge in ccm. n/400-P. V. S.-K-lösung. Um aus dem chlorierten Holzmehl seines Chlorlignin möglichst vollständig herauszulösen, ist es nötig wie in Tabelle 4 ersichtlich, das Holzmehl 30 Minuten lang mit 3% iger Natriumsulfitlösung zu erhitzen.

Bei Bestimmung der Gesamtcellulose nach Cross und Bevan wiederholt man im allgemeinen viermal Chlorierung und Erhitzung mit Natriumsulfit. Zielt man aber nur auf Entfernung des Lignins von Probe, ist es schon genug, die Wechselwirkung von Chlorgas und Natriumsulfit zweimal zu wiederholen.

d) Einfluss *p*H. Wert bei Kolloidtitration. — Da die Kolloidtitrationsmethode an

Bestimmung von dissoziierbaren Gruppen der Chlorligninsulfosäure geknüpft ist, so sind die Ergebnisse empfindlich gegen *p*H-Wert bei Titration. Bei verschiedenen *p*H-Werten führte ich die Titration durch. In Fig. 2 ist die Abhängigkeit des Polyaminverbrauchs von dem *p*H-Wert bei Titration gezeigt.

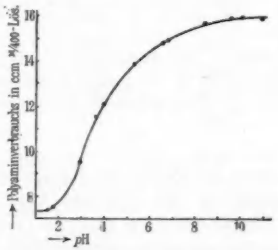

Fig. 2.—Die Abhängigkeit des Polyaminverbrauchs der in Chlorligninsulfosäure ("Sugi") von *p*H-Wert bei Kolloidtitration.

Der *p*H-Wert von Lösung wurde mit Glaselektrode bestimmt. Der Polyaminverbrauch verändert sich mit *p*H-Wert, aber bleibt konstant über *p*H 9. Wenn man die Titrierung deshalb bei über *p*H 9 ausführt, so kann man die gute Reproduzierbarkeit erhalten. Der Verfasser pflegt immer in Gegenwart von etwas Ammoniak zu titrieren.

Bestimmung der Bleichfähigkeit von Zellstoffen

Die bisherigen Methode zur Bestimmung der Bleichfähigkeit von Zellstoffen beruhen grossteneils auf der leichten Oxydierbarkeit des Lignins oder seiner Reaktionsfähigkeit gegen Chlor. Als das hauptsächlichste Oxydationsmittel kommen Hypochlorit-, Hypobromit- und Permanganatlösung in Frage. Um befriedigende Ergebnisse zu erzielen, muss man aber in dem meisten Fallen in genauer Festlegung der Versuchsbedingungen arbeiten. Wir müssen nun daher eine Methode suchen, die keine längeren Reaktionszeit und keine genaue Einhaltung so vieler Bedingungen in Anspruch nimmt. Die Kolloidtitration erfüllt auch diese Erfordernisse.

Wie bereits bekannt ist, liegt das Lignin in Sulfitzellstoff als Ligninsulfosäure vor, die in diesem Zustande in Alkali unlösich ist. Es wird aber, wie man öfter bei Bleichen von Sulfitzellstoff erfahrt, unter Einwirkung von Chlorgas in die Chlorligninsulfosäure chloriert, die in verdünnter Natronlauge leicht lösich ist. Auch das Lignin in Kraftzellstoff kann wie bei Holz durch Wechselwirkung von Chlorgas und Natriumsulit sehr leicht herausgelöst werden. Bei Zellstoffen ist die Herauslösung des Lignins wegen ihrer günstigen physikalischen Eigenschaften sehr leichter als bei Holzmehl.

a) Ausführung der Bestimmung.—Für Probe nimmt man 2.0 trockenen Zellstoff, den man mit wasser auffeuchtet oder eine 5 g. nasse, durch Hand ausgedrückte, ungefähr 60 % Wasser enthaltende Zellstoffprobe. Die Probe wurde in Glassfilter oder in Meyerkolben etwa 2 Minuten lang mit Chlorgas einwirken lassen.

Bei Sulfitzellstoff kann man das Chlorlignin bei Zimmertemperatur nur mit verdünnter Natronlauge vollständig extrahieren, weil sein Lignin schon als Ligninsulfosäure vorliegt. Der chlorierte Sulfitzellstoff wurde nach Absaugen von haftendem Chlorgas in Meyerkolben von 200 ccm. Inhalt eingeführt, in dem sich 100 ccm. n/20-NaOH befindet. Der Kolben wurde etwa 10 Sekunden lang kräftig durchgeschüttelt, um zu zerfassern und damit die Herauslösung der Chlorligninsulfosäure zu erleichtern. Dann wurde der Zellstoff auf einer Nutsche abfiltriert. Die so erhaltenen alkalischen Filtrat wurde mit einigen Tropfen der konz. Salzsäure neutralisiert und 10 ccm. dávon zur Bestimmung der Chlorligninsulfosäure benutzt, wobei n/200-M. G. Ch.- und n/400-P. V. S.-K-lösung dienten. Die Kolloidtitration wurde in Gegenwart von etwas Ammoniak ausgeführt. Je nach dem Gehalt an Chlorligninsulfosäure muss man so viel Menge Polyaminlösung zusetzen, dass mindestens das über 4 ccm. n/400 P. V. S.-K-lösung entsprechende Polyamin zurückbleibt, um die guten Reproduzierbarkeit zu erhalten.

Bei Kraftzellstoff muss man die chlorierte Probe in schwach alkalischem Medium mit 100 ccm. 3% iger Natriumsulfitlösung auf siedende Wasserbad 5 Minuten lang extrahieren. Um das Lignin von Kraftzellstoff quantitativ herauszulösen, muss man die Wechselwirkung von Chlorgas und Natriumsulfit zweimal wiederholen.

Durch erstmalige Extrahierung erhaltet man jedoch immer etwa 90% von dem Gesamtlignin. deshalb braucht man nicht die Extrahierung zweimal zu wiederholen. Indem man der erstmal extrahierte Menge des Lignins den Faktor 1.11 multipliziert, kann man gleich den Gesamtligningehalt der Probe erhalten.

Für die praktischen Bedürfnisse der Betriebskontrolle genügt es, dass man den Ligningehalt von 0.2 g. trockenem Zellstoff in ccm. n/400-Polyaminlösung angibt. Ich schlage für diese Zahl die Beseichnung "Polyaminzahl" vor. Tabelle 5 und Fig. 3 zeigen die Beziehung

Tabelle 5

Beziehung zwischen Polyaminzahl (PAZ) und Ligningehalt von Kraftzellstoff

Zellstoff Nr.	Die aus 2 g. lufttrockenem Zellstoff extrahierte Ligninmenge in ccm. n/400-P. V. S.-K				Ligningehalt nach 72%iger H_2SO_4-Methode, %	Ligninmenge in 2.0 g. lufttrock. Probe, mg.	Äquivalentgewicht von Lignin in Zellstoff	PAZ von Zellstoff
	erstmalige	zweitmalige	dritmalige	Gesamtsumme				
1	76.0	5.0	1.9	83	2.42	42.5	205	9.5
2	101.2	8.1	2.0	111	3.35	59.5	214	12.5
3	126.9	10.8	3.1	141	4.27	74.5	212	16.2
4	135.4	9.9	3.0	148	4.42	76.6	207	17.3
5	146.4	10.9	3.1	160	4.93	85.7	214	18.5
6	201.2	13.5	3.0	217	6.28	111.0	201	25.0
7	242.8	16.6	4.0	262	7.73	134.0	204	30.6

zwischen Polyaminzahl (PAZ) und Ligningehalt des Kraftzellstoffes. Zwischen PAZ und Ligningehalt (Klason-Lignin) ist ein enger Zusammenhang vorhanden. Rechnet man wie bei Holzlignin aus Ligningehalt des Klaftzellstoffes dessen Äquivalentgewicht gegen Alkylaminogruppe, so erhalt man die Ziffern in Tabelle 5 Spalte 6.

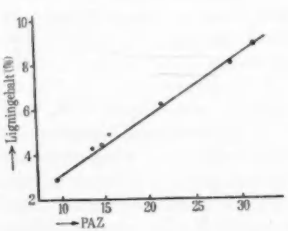

Fig. 3.—Beziehung zwischen PAZ und Ligningehalt des Kraftzellstoffes.

c) Einfluss der Veesuchsbedingungen auf Ergebnisse.—Der Verfasser untersucht zuerst die Abhängigkeit der Ergebnisse von Einwirkungszeit des Chlorgases, von der Menge und Konzentration der zur Extrahierung der Chlorligninsulfosäure gebrauchten Natronlauge und von dem *p*H-Wert bei Kolloidtitration.

Mit Ausnahme des Einfluss von *p*H-Wert sind die Ergebnisse von anderen Versuchsbedingungen unabhängig. Man erhalt denselben Wert, ganz gleich, ob die Einwirkungszeit von Chlorgas 2, 5, 10 oder 60 Minuten lang dauert. Polyaminzahl ist auch von Konzentration der Natronlauge unabhängig, die zur Extrahierung der Chlorligninsulfosäure in Sulfitzellstoff benutzt wird, wenn sie genug dick ist, um die infolge der Chlorierung gebildete Salzsäure zu neutralisieren. Der Gebrauch der zu dicken Natronlauge zur Herauslösung der Chlorligninsulfosäure ist aber nicht vorteilhaft, weil bei starker Salzlösung der Endpunkt der Kolloidtitration undeutlich wird.

Der Verfasser pflegt 100 ccm n/20 NaOH auf 2.0 g. trockenen Zellstoff zu benutzen. Die Reproduzierbarkeit der Ergebnisse ist sehr gut. Die Doppelbestimmung liegen innerhalb der Fehlergrenzen von 0.05 ccm.

Der *p*H-Wert bei Kolloidtitration hat auf Polyaminverbrauch einen grossen Einfluss, denn auch bei dem Lignin in Zellstoffen entsteht infolge der Chlorierung eine grosse Menge phenolische OH-gruppe. Bei verschiedenen *p*H-Werten führte ich die Kolloidtitration durch. In Fig. 4 und 5 ist die Abhängigkeit des Polyaminverbrauchs von dem *p*H-

Tabelle 6

Einfluss der verschiedenen Versuchsbedingungen auf Polyaminzahl

Konzent. der Natronlauge zur Extrahierung	n/10 8.20	n/20 8.20	n/40 8.00	n/60 7.98
Einwirkungsdauer von Chlorgas	2 Min. 8.18	5 Min. 8.22	10 Min. 8.00	60 Min. 8.00
Einwirkungstemp. von Chlorgas	0°C 8.20	15°C 8.20	30°C 8.20	
Häufigkeit von Extrahierung	einmal 8.18	zweimal 8.20		

Note: Die Ziffern in Tabelle zeigen die Polyamin-Zahl.

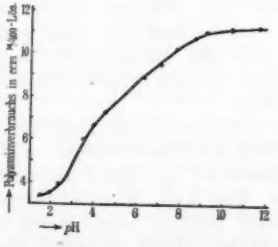

Fig. 4.—Die Abhängigkeit des Polyaminverbrauchs des Lignins in Sulfitzellstoff von dem *p*H-Wert bei Kolloidtitration.

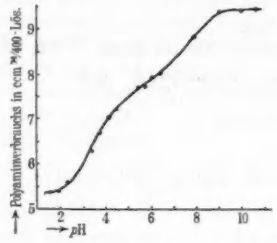

Fig. 5.—Die Abhängigkeit des Polyaminverbrauchs des Lignins in Kraftzellstoff von *p*H-Wert bei Kolloidtitration.

wert bei Titration gezeigt. Der Polyaminverbrauch nimmt zwar mit dem *p*H-Wert zu, aber bleibt konstant über *p*H 9. Wenn man die Titrierung deshalb bei über *p*H 9 ausführt, so kann man die gute Reproduzierbarkeit erhalten. Der Verfasser pflegt immer in Gegenwart von etwas Ammoniak zu titrieren.

In welchem Verhältnisse stehen nun die neu erhaltenen Wert zu den Zahlen der Oxydationsmethoden? Ich trug in dem Bild (Fig. 6) auf der Abszisse die Chlorverbrauchzahlen nach Sieber auf der Ordinat die Polyaminzahl auf.

Zwischen PAZ und Sieber-Zahl ist ein enger Zusammenhang vorhanden. Aus den Ergebnisse der neuen Methode kann man gleich den Ligningehalt des Probezellstoffes rechnen, wenn das polyaminverbrauch des anwesenden Lignins in Probezellstollen bekannt ist. Indem der Verfasser von dem Gewicht der Verbindung der Chlorligninsulfosäure mit G, Ch. oder M. G. Ch. das bekannte Gewicht des verwendeten Fällungsmittels abzieht, fand er direkt das Äquivalentgewicht des Lignins in Sulfitzellstoff. Nach seinem Versuche ist es etwa 213. Im früheren Mitteilung[7] rechnete der Verfasser aus der Polyaminzahl eines oulfitzellstoffes dessen Ligningehalt unter Annahme, dass das Lignin in Sulfitzellstoff dasselben Äquivalentgewicht (147) wie das des Lignins in Holz habe. Es ist jetzt mir deutlich worden, dass diese Annahme unrecht gewesen war. In Tabelle 7 ist der Ligningehalt der verschiedenen Sulfitzellstoffen nach verschiedenen Methoden gegenübergestellt.

Tabelle 7

Sieber-Zahl	Polyamin-zahl	Ligningehalt, % nach[8] Sieber	Ligningehalt, % berechnet aus Polyaminzahl
20.1	5.01	1.30	1.33
21.8	5.38	1.56	1.43
23.1	6.80	1.65	1.81
26.5	8.10	2.05	2.15
26.8	8.20	2.08	2.18
28.0	8.25	2.20	2.20
29.3	8.93	2.38	2.37

Wie aus Tabelle 7 ersichtlich ist, stimmt gut der aus PAZ berechnete Ligningehalt mit demjenigen nach Sieber überein.

Zum Schluss muss der Verfasser dem Herrn Prof. K. Nishida für seine freundliche Leitung, sowie Herren I. Sakata und M. Shimizu für ihren Beistand durch unermüdliche Arbeit den herzlichen Dank sprechen. Diese Arbeit wurde mit Unterstützung der Takatiho Papierzellstoff-Fabrik geführt, wofür ich an dieser Stelle Dank sagen möchte.

Institut für Wissenschaft und Industrie,
Kyushu Universität

(7) R. Senzyu, *Proc. Japan, Academy*, **28**, 304 (1952).
(8) Sieber, Schwalbe-Sieber, Die Betriebskontrolle in der Zellstoff- und Papierindustrie, S, 529 (1931).

Sterols and Other Unsaponifiable Substances in the Fats of Shell Fishes, Crustacea and Echinodermata. XI. Sterols in the Fat of Clam

By Yoshiyuki TOYAMA, Toru TAKAGI and Tatsuo TANAKA

(Received June 16, 1952)

Sterols in the fat of the clam, *Meretrix meretrix*, was studied in the 3rd report[1] of this series, and a sterol named meretristerol having m. p. 133—134.5°, and its acetate of m. p. 144—144.5° and the formula $C_{28}H_{46}O$ or $C_{29}H_{48}O$ was separated. But later in the 9th report[2] it was revealed that the meretristerol previously obtained was impure, since repeated recrystallizations of the steryl acetate gave a fraction of m. p. 149.5° which was believed to be pure meretristeryl acetate. Saponification of this acetate gave meretristerol of m. p. 144.5°. Meanwhile, Bergmann and Ottke[3] suggested that meretristerol is not a single sterol but a mixture of brassicasterol and chalinasterol.

With the purpose of obtaining pure meretristerol in a sufficient quantity to permit a further study, the sterol mixture was separated from the fat extracted from another lot of clams, and its acetate was subjected to repeated recrystallizations. There was obtained a fraction of m. p. 149°, but its melting point was raised somewhat promptly by further recrystallizations until a fraction of m. p. 173—174° was finally obtained in a very small quantity. Accordingly, it must be recognized that even the meretristerol described in the 9th report was not a pure single sterol. Also the fraction of high melting point, 173—174°, was not considered to be a single acetate from the results of the fractionation of its bromide.

The acetate mixture after removal of the high melting fraction was brominated in ether solution and the product was separated into the ether insoluble bromide (I) and the ether soluble bromide (II). The bromide I was then treated with chloroform-ethanol and ethanol, and there were obtained two fractions (Ia) and (Ib). The bromide II was treated with ethanol and a fraction melting at 120—123° was separated. Debromination of this fraction and

Table 1

	Sterol		Acetate		Benzoate		Acetate tetrabromide		Acetate dibromide	
	m. p., °C.	$[\alpha]^{\circ}_{D}$	m. p., °C.	$[\alpha]^{\circ}_{D}$	m. p., °C.	$[\alpha]^{\circ}_{D}$	m. p., °C.	$[\alpha]^{\circ}_{D}$	m. p., °C.	$[\alpha]^{\circ}_{D}$
Sterol from bromide Ia	145	−63.8	151	−60.7	158	—	202	−43.8	215—216	—
Brassicasterol[4]	146	−61.1	152	−65	163	−35[5]	205	—	236—238	—
Sterol from bromide Ib	154	−53.3	146—147	−52.1	140	−21.7	192	−42.5	213—214	—
Poriferasterol[6]	155—156	−49.7	146.5—147	−53	139.5—140.5	−21.9	192	−43.5	211—212	−31
Sterol from fraction III	136—137	−39.3	137—138	−38.2	133—135	−21.2				
Clionasterol[7]	137.5—138.5	−37	137	−41.9	134.5—135	−16.8				
Sterol from fraction IV	142	−37.6	114	—	145	−15.8				
Cholesterol	148	−38	114	−43	146	−17				

(1) Y. Toyama and M. Yajima, *J. Chem. Soc. Japan*, **64**, 878 (1943).
(2) M. Kita, I. Naka and Y. Toyama, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **71**, 21 (1950).
(3) W. Bergmann and R. C. Ottke, *J. Org. Chem.*, **14**, 1085 (1949).
(4) E. Fernholz and H. E. Stavely, *J. Am. Chem. Soc.*, **61**, 142 (1939); **62**, 428 (1940).
(5) l. c., (3).
(6) F. R. Valentine, Jr. and W. Bergmann, *J. Org. Chem.*, **6**, 432 (1941); W. Bergmann and R. J. Feeney, ibid., **14**, 1078 (1949); W. Bergmann, F. H. McTigue, E. M. Low, W. M. Stokes and R. J. Feeney, ibid., **15**, 96 (1950).
(7) F. R. Valentine, Jr. and W. Bergmann, *J. Org. Chem.*, **6**, 432 (1941).

fractional crystallization of the debrominated product gave two fractions (III) and (IV). On examining each fraction, brassicasterol and poriferasterol were obtained from the bromides Ia and Ib respectively, while the fractions III and IV were found to contain clionasteryl acetate and cholesteryl acetate respectively. The properties of sterols obtained from each fraction are given in Table 1.

The occurrence of brassicasterol in the sterol components of Pelecypoda[8] had already been known, but poriferasterol had not yet been found in shell fish. Clionasterol was also found in Pelecypoda for the first time by the present study, though its occurrence in Gastropoda[9] had been known.

The acetate of m. p. 173—174° was brominated, the bromide separated into two fractions, and each fraction debrominated. The debromination products from each fraction had considerably lower melting points than the original acetate. Thus the original acetate was not regenerated by the debromination of the bromide. Accordingly the original acetate must have undergone isomerization or other changes in bromination and debromination cycle.

Experimental

Clams used in the present experiments were procured from the Shimono-isshiki Fishery Co-operation, Nagoya, in April and May, 1950. Thirty-six kg. of wet meat obtained from 150 kg. of clams was dried below 80° under vacuum, and the dried material (4.58 kg.) was reduced to powder, from which 462 g. of fat (10.1% of dried material) was extracted using trichloroethylene. Saponification of the fat and extraction of the soap solution with ether in the usual way yielded 83 g. of unsaponifiable substance (18.0% of fat), which was a mixture of crystalline solid and viscous oily liquid of dark reddish orange color.

Recrystallization of Steryl Acetate. — The unsaponifiable substance was recrystallized three times from ethanol, and there was obtained 27.1 g. of crystalline solid of m. p. 118—138°, which was acetylated by refluxing with acetic anhydride. The acetate (30.2 g.) was recrystallized five times from ethanol, once from acetone-ethanol, and twice from acetone, giving an acetate (4.5 g.) of m. p. 129—132°, $[\alpha]_D^{18}$ −40.3°, saponification value 131.1 and iodine value (pyridine sulfate dibromide method) 98.0. Further recrystallizations of this acetate were carried out as shown in Table 2.

Table 2

Recrystallized from	Acetate crystallized out		Acetate in mother liquor
	Yield, g.	m. p., °C.	m. p., °C.
Benzene-ethanol	3.0	132—135	130—132
Acetone	0.4	142—149	129—130(a)
〃	0.2	165—167	131—132
〃	0.12	173—174	155—158
(a) 2.6 g., $[\alpha]_D^{18}$ −41.5°, saponification value 128.3, iodine value 97.0. This fraction of the acetate from the mother liquor was subjected to further recrystallizations as shown below.			
Benzene-ethanol	2.0	131—134	130—132
Acetone	1.2	136—141	128—132
Ether-ethanol	0.5	144—149	130—132
Acetone	0.33	145—149	132—134
〃	0.19	146—149	138—139
〃	0.16	148—149.5	142—143.5
〃	0.13	170—171	145—146
〃	0.11	173—174	145—149

Fractionation of Acetate Bromide.—Acetate contained in the mother liquors of recrystallizations was recovered, and two fractions (A) 4.9 g., melting between 130° and 135°, and (B) 12 g., melting between 110° and 130°, were separated. Both fractions were brominated and bromides were fractionated in the following way. Fraction A was dissolved in 80 cc. of ether, and bromine in ether (5 g. in 20 cc.) was added dropwise under cooling at −10°. After keeping the solution at −10° for 20 hours, 1.4 g. of insoluble bromide (I) was filtered, washed twice with ether using 50 cc. each time, and then recrystallized four times from 20 cc. of chloroform-ethanol, by which there was obtained 0.12 g. of crystalline bromide (Ia). The chloroform-ethanol filtrate was added with ethanol, the precipitated bromide (0.2 g.) was filtered, and the filtrate was added with a further large quantity of ethanol, by which 0.8 g. of solid bromide (Ib) was precipitated. Fraction B yielded a very small amount of insoluble bromide by bromination in ether. The combined ether filtrate from fractions A and B was treated with sodium bisulfite solution for the removal of excess bromine, washed with water, dried over anhydrous sodium sulfate, and concentrated to a small volume by distilling ether. On adding ethanol to the concentrated ether solution, the bromide was fractionally precipitated, and there were obtained 7.4 g. of a fraction melting at 120—123° together with fractions of m. p. 175—180°, 110—114° and oily liquid.

Bromide Ia. — m. p. 202°, $[\alpha]_D^{18}$ −43.8°, Br 41.73% (calculated for $C_{29}H_{46}O_2Br_4$: Br, 42.04%). This bromide was debrominated with zinc and acetic acid. The debrominated product, after recrystallization from ethanol, had m. p. 151° and $[\alpha]_D^{18}$ −60.7°. It showed no depression of melting point when mixed with brassicasteryl acetate, m. p. 151—152°, prepared from rape oil in this laboratory. Saponification of the acetate gave

(8) l. c., (3); T. Matsumoto and Y. Toyama, *J. Chem. Soc. Japan*, **65**, 238, 310 (1944).

(9) C. A. Kind and S. C. Herman, *J. Org. Chem.*, **13**, 867 (1948).

free sterol which, after recrystallization from ethanol, had m. p. 145° and $[\alpha]^{18}_D$ −63.8°. Free sterol was added with benzoyl chloride in pyridine, kept for 24 hours at room temperature, and then water was added. The precipitated benzoate was washed with water and then recrystallized four times from acetone. It melted at 158°. A portion of the bromide Ia was partially debrominated by potassium iodide.[10] The product, dibromide, melted at 215—216° after recrystallizing several times from ethanol.

Bromide Ib.—m. p. 192° (with decomp.), $[\alpha]^{18}_D$ −42.5°, Br 41.46% (calculated for $C_{31}H_{56}O_2Br_4$: Br, 41.33%). This bromide was debrominated with zinc and acetic acid. The product, after recrystallization from ethanol, had m. p. 146—147°, $[\alpha]^{18}_D$ −52.1° and saponification value 124.7 (calculated for $C_{31}H_{56}O_2$ 123.4). Saponification of the acetate yielded free sterol which, after recrystallization from ethanol, had m. p. 154° and $[\alpha]^{18}_D$ −53.3°. Benzoylation of free sterol gave a benzoate of m. p. 140°, $[\alpha]^{18}_D$ −21.7° and saponification value 110.5 (calculated for $C_{38}H_{52}O_2$ 108.6). Dibromide obtained by partial debromination of the bromide Ib had m. p. 213—214° and Br 27.24% (calculated for $C_{31}H_{56}O_2Br_2$: Br, 26.05 %).

Sterol from Fraction III.—The ether soluble bromide of m. p. 120—123° was debrominated with potassium iodide in ethanol, whereby the debromination occurred nearly quantitatively yielding a product which had less than 0.1% of bromine. Accordingly, the bromide of m. p. 120—123° is considered to contain only a minute amount, if any, of compound having bromine in its side chain. On debromination of this bromide with zinc and acetic acid, there was obtained an acetate of m. p. 131° and $[\alpha]^{17}_D$ −38.2°. Recrystallizing twice from acetone, it had m. p. 137—138° and $[\alpha]^{17}_D$ −38.2°. The melting point was unaltered by further recrystallization. Saponification of this acetate and recrystallization of the product from acetone yielded a free sterol of m. p. 136—137° and $[\alpha]^{17}_D$ −39.3°. The benzoate prepared from this sterol had m. p. 133—135°, $[\alpha]^{17}_D$ −21.2° and saponification value 108.3 (calculated for $C_{36}H_{54}O_2$ 108.1). On solidifying the melted benzoate, it developed a blue coloration at 130—110° as is the case with clionasteryl benzoate[11].

Sterol from Fraction IV.—The acetate contained in the acetone mother liquors of recrystallizations of the acetate fraction III was saponified, the resulting free sterol was benzoylated, and the benzoate was recrystallized three times from acetone. The product had m. p. 145° and $[\alpha]^{17}_D$ −15.8°. Saponification of the benzoate yielded free sterol having m. p. 142° and $[\alpha]^{17}_D$ −37.6° after recrystallization from ethanol. The acetate prepared from this sterol had m. p. 114° after recrystallization from ethanol.

The Acetate of m. p. 173—174°.—The high melting acetate obtained by the final recrystallization recorded in Table 2 had $[\alpha]^{17}_D$ −62.5° and saponifacation value 123.9. The bromination product of this acetate was separated into two fractions, m. p. 172—174° (with decomp.) and m. p. 115—125°, by means of ethanol. The fraction of m. p. 172—174° (with decomp.) had Br 38.71%. Debromination of this fraction with zinc and acetic acid yielded a product which had m. p. 143° after three recrystallizations from ethanol. The fraction of m. p. 115—125° had Br 26.10%. Debromination of this fraction yielded a product which had m. p. 136° after two recrystallizations from ethanol.

Summary

(1) Steryl acetate obtained from clam fat was recrystallized from several different solvents, and it was found that the acetate recorded in the previous report as pure meretristeryl acetate, m. p. 149.5°, was not a pure single compound. Final recrystallization gave an acetate of m. p. 173—174°, though in a very small yield.

(2) Acetate mixture after removal of the fraction of m. p. 173—174° was fractionated by way of bromide, and it was found that brassicasterol, poriferasterol, clionasterol and cholesterol are present among the sterol components of clam fat.

(3) Bromination of the acetate of m. p. 173—174° and debromination of the bromination product yielded acetate having considerably lower melting points than the original acetate. Accordingly, there must have occurred isomerization or other changes in bromination and debromination cycle.

The expense of the present study has been defrayed from the Grant in Aid for Fundamental Scientific Research.

Department of Applied Chemistry,
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(10) E. Fernholz and H. E. Stavely, *J. Am. Chem. Soc.*, **62**, 428 (1940).
(11) l. c., (7).

Rheology of Coal. III. A Structural Interpretation of Coal Oxidation from the Internal Viscosity Variations

By Katsuya INOUYE

(Received July 22, 1952)

Introduction

Many results have been reported on the phenomenon that the caking properties of coal are markedly changed by oxidation. R. V. Wheeler and others[1] have shown that even a degree of oxidation insufficient to affect the ultimate analysis reduces the caking properties profoundly. J. D. Davis and his co-workers[2] have reached the same conclusion by their own methods. In other cases, however, it is known that the caking properties can increase by mild oxidation.[3] These experimental facts, apparently contradictory, are readily understood, as H. L. Riley and his collaborators[4] have suggested, when it is accepted that the addition of oxygen to the coal molecules strengthens the intermolecular forces and results in restricting the mobility of the turbostratic system, so that excess of plasticity during carbonization, which may make the weak coke too porous, can be reduced; on the other hand, the appropriate plasticity of the caking coal at the caking temperatures is destroyed by further addition of oxygen atoms.

The author has shown from Young's modulus experiments[5] and the internal viscosity measurements[6] by vibrational methods that the caking properties of coal may be explained by these rheological factors and has proposed a theory on the structure and physical properties of coal. If the proposed theory on the difference between the structures of strongly-caking coal and weakly- or non-caking coal is valid, the corresponding variations in rheological properties should be observed experimentally by oxidation when the strongly-caking coal changes to a less-strongly caking coal. The mechanism of coal oxidation may also be discussed from the rheological standpoint. This report describes the internal viscosity variations during air-oxidation of several typical coals.

Description of Samples and Experimental Method

The coals used in this report are chosen from the same species examined in the preceding experiments, and Table 1 describes some common characteristics of the samples.

The experimental method for measuring the internal viscosity is described in the preceding paper.[6] All specimens were cut parallel to the bedding plane, in rectangular bars with accuracy of 1% in each dimension. The resonance curves between amplitude and frequency were obtained with fixed-free bar specimens at 30.0°C. and at the resonant frequency in the range of 1200~1400 c/sec. and hence the internal viscosity values were calculated according to the relations between vibrational decrement factor and viscosity,

Table 1

Description of Samples

Sample	Origin	Classification	Caking Property	Volatile Matter, Mean Value (dry, ash-free basis) in %
Takashima	Kyushu, Japan	Bituminous	Strongly-caking	38
American	U. S. A.	Bituminous	Strongly-caking	35
Toro	Saghalien, U. S. S. R.	Bituminous	Weakly-caking	46
Yubetsu	Hokkaido, Japan	Producer gas coal	Non-caking	64
Shosaku	China	Anthracite	Non-caking	7.7

(1) R. V. Wheeler and T. G. Woolhouse, *Fuel*, **11**, 44 (1932).
(2) L. D. Schmidt, J. L. Elder and J. D. Davis, *Ind. Eng. Chem.*, **32**, 548 (1940); R. E. Brewer, C. B. Holmes and J. D. Davis, *Ind. Eng. Chem.*, **32**, 930 (1940).
(3) L. D. Schmidt, J. L. Elder and J. D. Davis, *Ind. Eng. Chem.*, **28**, 1346, (1936); T. Iwasaki et al., Annual Meeting, *Chem. Soc. Japan*, 1950.
(4) H. E. Blayden, J. Gibson and H. L. Riley, *Proc. Conf. Ultra-fine Structure of Coals and Cokes, London*, **1944**, 176.
(5) K. Inouye, *J. Colloid Sci.*, **6**, 190 (1951).
(6) K. Inouye, This Bulletin, **26**, 84 (1953).

$$\eta = \frac{2\lambda n \rho l^4}{\kappa^2 m^4}, \qquad (1)$$

and

$$\lambda = \frac{\pi \Delta n}{\sqrt{3}\, n}, \qquad (2)$$

where, η = internal viscosity, λ = logarithmic decrement, n = resonant frequency, ρ = density of the specimen, l = length of the specimen, κ = radius of gyration of cross section, m = a factor corresponding to the mode of vibration, and Δn = the half value breadth of the resonance curve at the resonant frequency.

The measurement was carried out at first on the original (no oxidation) sample and then it was replaced into an air oven regulated at 120°C. for air-oxidation. The air was introduced from the bottom of the oven and went out of the top through a metal rack on which the specimens were set. After 30 hours' oxidation, the sample was taken out of the oven, cooled to the room temperature and fitted for vibrational measurements. The experiment was repeated after 30 more hours' oxidation (oxidized for 60 hours in total). The cement supporter had sometimes to be renewed after oxidation for the specimen separates from the supporter by heating. The change of dimensions of the specimens was considered sufficiently small, so that the dimensional factors (length and thickness) in Equations 1 and 2 were kept constant even after the oxidation. The change of weight of the specimen remained within 1%.

Changes of Caking Properties by Oxidation

The grains having diameter of approximately 0.5 cm. of each sample were prepared and oxidized in the same oven at 120°C. This diameter preferred was the mean thickness, i. e., the minimum dimension which may determine the oxidation velocity, of the specimen. Table 2 shows the changes of oxygen contents for four coals after 60 hours' oxidation. The moisture and ash contents listed are based on 76% humidity, the ultimate analysis on dry basis. The oxygen increases rather remarkably by the oxidation.

Table 3 shows the changes of the amount of extractable portion by pyridine on the existence of which the strong caking properties of the coals depend, and of the Lessing index. The pyridine extraction was carried out by the Soxlet method and the content was calculated in dry-ash-free bases, from the weight of α portion (steam distilled and dried). The Lessing caking index is a ratio of the height of carbonized sample after heating for 7 minutes at 900°C. in a silica retort to the height of 1 g. of the original coal of minus 100 Tyler mesh.

These changes seem to show that the oxidation method in this experiment can add oxygen to the coals and make the caking properties decrease. A recovery of the extraction data after 60 hours' oxidation may suggest, as explaind later, the decomposition in the coal samples.

Internal Viscosity Changes by Oxidation

As already reported in the preceding articles,[5][6] Young's modulus, E, and internal viscosity, η, of coal are respectively linear functions of ash volume concentration, ϕ,

$$\eta = \eta_0(1 + K'\phi) \qquad (3)$$

Table 2

Changes of Oxygen Contents

Sample	Moisture	Ash	H	C	N	O and etc.	O and etc. (dry-ash-free)
Original Coals:							
Takashima	2.42	7.25	5.36	77.30	1.38	15.96	17.24
American	1.79	10.65	5.36	76.83	1.67	16.14	16.28
Yubetsu	4.98	11.83	5.36	67.94	1.17	25.53	29.16
Shosaku	4.50	9.29	2.31	82.27	0.91	14.51	16.07
After 60 Hours' Oxidation:							
Takashima	2.65	4.44	5.38	76.63	1.44	16.55	18.38
American	1.71	14.66	4.67	70.83	1.75	22.75	26.74
Yubetsu	3.64	17.29	5.15	63.83	1.17	29.85	36.11
Shosaku	3.79	11.05	2.33	81.18	1.08	15.41	17.41

Table 3

Changes of Properties

	Takashima			American		
	0 hour	30 hours	60 hours	0 hour	30 hours	60 hours
Extracted Portion, %, Dry-ash-free Bases	11.5	0.03	1.8	8.6	0.005	0.14
Lessing Index	3.14	1.18	1	4.99	3·84	—

and

$$E = E_0(1 + K\phi) \qquad (2)$$

where, E_0 and η_0 show the rheological values of "pure" coal molecules and K and K' represent the solvation factors of coal molecules with ash. Small E_0 and η_0 as well as large solvation factors distinguish the strongly-caking coals. The internal viscosity and ϕ relationship of the original coals is shown in Fig. 1, which also contains several data published in the preceding paper.[6] The detailed description of the curves especially minima and maxima which appeared for the caking coals will be given in the following article.* Figs. 2 and 3 show the internal viscosity values after 30 and 60 hours' oxidation. The values of η_0 and K' of the coals both before and after 30 hours' oxidation are given in Table 4.

The variations of the internal viscosity by oxidation are as follows: (1) the inclination of the linear relationship becomes flat, (2) the internal viscosity

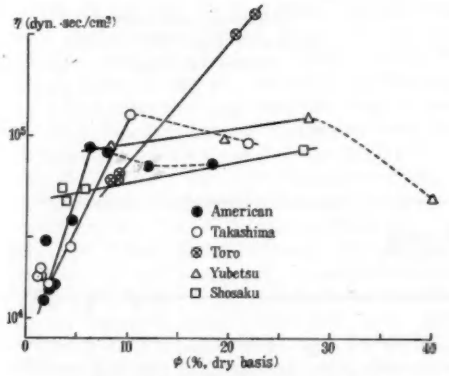

Fig. 1.—Internal Viscosity and Ash Content. Original Coals.

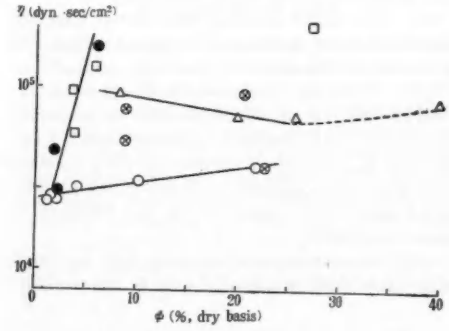

Fig. 2.—Internal Viscosity and Ash Content. Oxidized Coals for 30 hours.

* Rheology of Coal. VI. Unpublished work by K. Inouye and H. Tani.

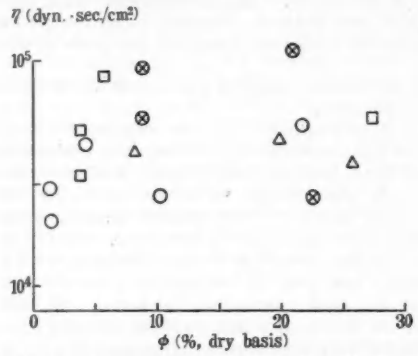

Fig. 3.—Internal Viscosity and Ash Content. Oxidized Coals for 60 hours.

Table 4

Changes of η_0 and K' by Oxidation

Sample	Duration of Oxidation: 0 hour		30 hours	
	η_0, c.g.s.	K'	η_0, c.g.s.	K'
American	1×10^3	16	2×10^4	0.95
Takashima	3×10^3	3.5	4.5×10^4	1.8×10^{-2}
Toro	2.3×10^4	2.7×10^{-1}	—	—
Yubetsu	8.4×10^4	1.0×10^{-2}	1.0×10^5	-6.1×10^{-3}
Shosaku	6.8×10^4	1.3×10^{-2}	—	—

value at $\phi=0$ increases, and (3) further oxidation (see Fig. 3) appears to destroy the definite relationship between molecules and inorganic ash. The experimental facts suggest that the rheological conditions in strongly-caking coals change to those in weakly- or non-caking coals, i. e., the free molecules which act as a plasticizer when the coal is carbonized, obtain stronger intermolecular forces by adding the oxygen atoms, so that the micelle structure by solvation becomes indefinite.

It may be interesting to note that the changes of viscosity for Takashima coal, which showed rapid decrease of the Lessing index by oxidation, were more remarkable than in the case of American coal, although the values for the latter sample after oxidation are not many for the brittle nature of the specimens.

When the oxidized coal, originally strongly-caking, is carbonized in the coke oven, the coal cannot fuse and swell at the caking temperatures of the original coal, say at 400~500°C., because of the too strong intermolecular interactions of the matrix (bitumen) molecules of the micelle system.

Discussions

These facts may give the interpretation of the mechanism of coal oxidation, as suggested by H. L. Riley et al., that the addition of oxygen to the coal molecules causes an increase of forces between molecules and hence a decrease of the

caking properties. The experiments may also support the author's proposed theory on the mechanism of caking properties and coal structure.

Some possible causes of the experimental errors are considered.

(1) Dependence of η on the frequency. The η values are influenced by the frequency measured. The author, however, cannot state the dependence, although some results have been given in the preceding report.(7) The causes of experimental difficulty for adjusting the frequency were in the fact that the correction of the dimensions of the oxidized specimens by re-shaping was very difficult for weak mechanical property, and that there is doubt that the oxidized layers of the specimen may be removed by re-shaping. The measurements, therefore, had to be carried out at the frequency range of 1200~1400 c/sec., notwithstanding the fact that the resonance frequency of an oxidized specimen decreases in most cases.

(2) Homogeneity of oxidation. It is known that the oxidation does not proceed homogeneously when the blocks are oxidized, but the oxidized layer may be formed to prevent further oxidation. In this experiment this point is not considered and the oxidation was presumed to be homogeneous.

(3) Decomposition of coal. The decomposition of coal during oxidation was mentioned above, and the influence of decomposition upon the changes of weight, density and ash concentration of the specimen is considerable. These factors, however, were maintained constant in calculation as the weight decrease after even 60 hours' oxidation was within 1%. The most important influence of the decomposition is in the fact that the decomposition may make internal flaws by which occurence the internal viscosity values increase. The consideration of internal flaws on the rheological properties will be reported in future articles concerning the rheological studies of coke.

The autho.'s thanks are due to Hideo Tani for helpful assistance in the experiment. He is also indebted to Dr. M. Kurokawa and Mr. A. Baba (this Institute) for interest in the rheological study of coal.

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(7) Reference 6 and the Report of the Fuel Research Institute, No. 66.

LETTER

On the Equilibrium between Radon and Radium and Radium B in Radioactive Mineral Waters

By Shunji UMEMOTO

(Received October 23, 1952)

From April, 1951 to March, 1952, the author measured continuously the variation of the contents of radium, radon, etc. in a spring called Hisui-no-Yu, at Misasa, Tottori, Japan; and it was found that when the amount of flow increased, the water temperature rose, the content of radon increased and the contents of radium and other common elements decreased. From these results, however, it was difficult to find any explanation for the formation and structure of this spring.(1)

Therefore, from February, 1952, the author measured continuously the radium radon, radium B and chloride content, the amount of flow and the water temperature of Hisui-no-Yu and three other springs at Misasa and the followingresults ware obtained:

(1) The radon content was higher than the valvue which would be expected from the equilibrium between radium and radon.(2)

(2) At times, the radium B content exceeded the value which would be expected from the equilibrium between radon and radium B. It is very interesting that, on some occasions, the equilibrium between such short-lived radioactive elements is not retained in mineral waters.

Further studies of this work will be made and more detailed results will be given later.

(1) S. Umemoto, *J. Chem. Soc. Japan*, **73**, 756 (1952) etc.

(2) This result was the same as that obtained already by the author and other investigators and the radium content varied with the chloride content as reported previously.

The author wishes to express his sincere thanks to Prof. K. Kimura of Tokyo Univ. for his kind guidance and encouragement.

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Resolution of a Sterically Hindered Stilbene Derivative, 4-Amino-3′-bromo-α′-chloro-α, 2′, 4′, 6′-tetramethylstilbene

By Michinori ŌKI

(Received January 30, 1953)

The author and Y. Urushibara[1] deduced the non-planar structures of α, α′-disubstituted stilbene derivatives from their ultraviolet absorption. If one of the rings is sterically hindered from rotating over the central substituted vinylene group and substituted unsymmetrically, then the stilbene derivative is expected to exist in optical enantiomorphs.

The author synthesized 4-amino-3′-bromo-α′-chloro-α, 2′, 4′, 6′-tetramethylstilbene, $4\text{-}H_2NC_6H_4CMe{=}CClC_6HBrMe_3\text{-}3',2',4',6'$, and resolved it by means of *d*-camphorsulfonic acid. The benzoyl derivative of the resolved amine showed m. p. 159—160° and $[\alpha]_D^{26}$ +56.1°. The enantiomorph was not isolated. This is the first example of an optically active stilbene derivative containing no asymmetric carbon atom.

Experimental Part

4-Nitrobenzyl 3′-bromo-2′, 4′, 6′-trimethylphenyl ketone (I).—$4\text{-}O_2NC_6H_4CH_2COC_6HBrMe_3\text{-}3',2',4',6'$. Powdered anhydrous aluminum chloride (15 g.) was added gradually to a boiling solution of bromomesitylene[2] (20 g.) and *p*-nitrophenylacetyl chloride[3] (20 g.) in carbon bisulfide (150 cc.), and the mixture was heated for 30 minutes, and treated with ice and hydrochloric acid. After standing overnight the solid was recrystallized from alcohol with use of active charcoal. Nearly colorless needles melting at 121.5—123° (yield 15 g.). Found: N, 3.95. Calculated for $C_{17}H_{16}O_3NBr$: N, 3.87%.

α-(4-Nitrophenyl)ethyl 3′-bromo-2′, 4′, 6′-trimethylphenyl ketone (II).—$4\text{-}O_2NC_6H_4CHMeCOC_6HBrMe_3\text{-}3',2',4',6'$. I (10 g.) and a solution of metallic sodium (0.7 g.) in absolute alcohol (20 cc.) were heated to a homogeneous solution, then with addition of methyl iodide (4.3 g.) to neutral reaction, and poured into water (100 cc.). Alcohol was evaporated under diminished pressure and the remainder was shaken with ether. The ether solution was washed with aqueous sodium thiosulfate, dried, and evaporated. The residue solidified and was recrystallized from alcohol-acetone. Pale yellow leaflets melting at 125—126° (yield 8 g.). Found: N, 3.72. Calculated for $C_{18}H_{18}O_3NBr$: N, 3.72%.

4-Nitro-3′-bromo-α′-chloro-α, 2′, 4′, 6′-tetramethylstilbene (III).—$4\text{-}O_2NC_6H_4CMe{=}CClC_6HBrMe_3\text{-}3',2',4',6'$. II (12 g.) was dissolved in phosphorus oxychloride (60 cc.), phosphorus pentachloride (30 g.) was added, and the mixture was heated on a waterbath for 2 hours. The cooled reaction mixture was treated with ice water and the formed viscous substance was recrystallized from alcohol-acetone. (The mother liquor gave a hardly solidifiable mass, presumably the cis-isomeride.) One more recrystallization from acetone gave pale yellow prisms melting at 92—93° (yield 6 g.). Found: N, 3.59. Calculated for $C_{18}H_{17}O_2NClBr$: N, 3.55%.

4-Amino-3′-bromo-α′-chloro-α, 2′, 4′, 6′-tetramethylstilbene (IV).—$4\text{-}H_2NC_6H_4CMe{=}CClC_6HBrMe_3\text{-}3',2',4',6'$. III (7 g.) was heated with tin (10 g.) and alcohol (50 cc.) on a waterbath, concentrated hydrochloric acid (10 cc.) diluted with alcohol (10 cc.) was added gradually, and the mixture was heated until no violet coloration occurred on adding one drop to alcoholic potash. Alcohol was evaporated under reduced pressure, the residue was decomposed with 5% aqueous caustic soda, and the separated oil was collected. The amine, being uncrystallizable, was benzoylated for characterization. Colorless fine crystals melting at 159—160°. Found: N, 3.11. Calculated for $C_{25}H_{23}ONClBr$: N, 2.99%.

Dextro-rotatory Benzoyl Derivative from the Amine (IV).—A solution prepared by dissolving the free amine (IV) (3 g.) in an aqueous acetone solution of *d*-camphorsulfonic acid (5 g.) gave an oily deposit on cooling which solidified in a time. Recrystallization from water-acetone containing a small amount of *d*-camphorsulfonic acid to a constant melting point or rotation (three recrystallizations usually) gave colorless plates melting at 140°. Found: N, 2.42. Calculated for $C_{26}H_{23}O_4SNClBr$: N, 2.35%. $[\alpha]_D^{26}$ +272.8° (0.0247 g. in 6 cc. alcoholic solution, α_D^{26} +1.14°).

The recrystallized *d*-camphorsulfonate was decomposed with 10% aqueous caustic soda. The uncrystallizable free amine was benzoylated with benzoyl chloride and pyridine, and the product was recrystallized from benzene-petroleum ether. Colorless fine crystals melting at 159—160°. Found: N, 2.96. Calculated for $C_{25}H_{23}ONClBr$: N, 2.99%. α_D^{26} of 0.0627 g. of the substance in

(1) This Bulletin, **25**, 109 (1952); Also see M. Oki, ibid., **25**, 112 (1952); **26**, 37 (1953).
(2) R. Adams and H. A. Stearns, "Organic Syntheses", Vol. XI, p. 24.
(3) E. Wedekind, *Ann.*, **378**, 289 (1911).

4 cc. alcoholic solution was found +0.88°. $[\alpha]_D^{26}$ +56.1°.

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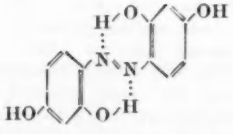
2,4,2',4'-Tetrahydroxyazobenzene, Synthetic Estrogen of a New Type

By Yoshiyuki URUSHIBARA and Takeyoshi TAKAHASHI

(Received January 31, 1953)

The authors synthesized 2,4,2',4'-tetrahydroxyazobenzene (4,4'-azoresorcinol), $2,4\text{-}(HO)_2C_6H_3N{=}NC_6H_3(OH)_2\text{-}2',4'$, expecting that it might be estrogenic, because it might have a chrysene-shaped, rigid ring system by virtue of double chelation and thus its molecular shape might resemble those of potent natural and synthetic estrogens, except that it would be quite flat:



The diazo-oxide from 4-aminoresorcinol 1-benzoate, $C_6H_3(OCOC_6H_5)(OH)(NH_2)$-1,3,4, was coupled with resorcinol. 2,4,2',4'-Tetrahydroxyazobenzene 4-benzoate was obtained in yellow fine crystals melting at 235°. Saponification gave the desired tetrahydroxyazobenzene in orange-colored crystals. It did not melt at 300° but gradually turned black.

Estrogenic activity of the tetrahydroxyazobenzene was examined by the vagina smear test with ovariectomized mice, the substance in oil being injected subcutaneously in two portions. A weighed amount dissolved in acetone was mixed with camellia oil and acetone was evaporated up. The substance partly separated out in suspension. 20 γ produced full estrus in 100% animals, and 10 γ in 60%. By the same test method 1 mg. of 4,4'-dihydroxyazobenzene[1] showed full action in 80% animals, and 500 γ in 20%.

The presumed position of the coupling was *a priori* very probable, because W. Will and W. Pukall[2] obtained 2,4-dihydroxyazobenzene as the main product by coupling benzenediazonium chloride with resorcinol. H. Kauffmann and W. Kugel[3] obtained the same 2,4-dihydroxyazobenzene by coupling benzenediazonium chloride with resorcinol monobenzoate and saponifying the formed 2-benzoate. The present authors coupled the diazo-oxide from 4-aminoresorcinol 1-benzoate with resorcinol monobenzoate. The product should be 4,2'-dibenzoate of 2,4,2',4'-tetrahydroxyazobenzne by analogy. The substance obtained by saponification was the same in every respect as the tetrahydroxyazobenzene synthesized by using free resorcinol, but owing to the infusibilty of the substance it was impossible to identify both specimens by a mixed melting point.

The considerably strong action of the tetrahydroxyazobenzene provides a strong evidence for the structure consisting of the four hydroxy groups at 2,4,2',4'-positions and the formation of the chelate rings. Extra hydroxy groups introduced into natural or synthetic estrogens have hitherto always diminished activity to a great extent. The fact that the two more hydroxy groups at 2,2'-positions give the tetrahydroxyazobenzene an activity very much stronger than that of 4,4'-dihydroxyazobenzene proves that they form chelate rings with the azo nitrogen atoms and thus constitute a molecular structure, rigid and similar to those of strong natural and synthetic estrogens.

The 2,4,2',4'-tetrahydroxyazobenzene is an estrogen of a new type in that the molecular structure favorable for estrogenic activity is formed by chelation. But, as it is quite flat, such a potency as is comparable with that of diethylstilbestrol or hexestrol cannot be expected.[4]

Experimental Part

A 10% aqueous solution of sodium nitrite was added gradually to a solution of 4-aminoresorcinol 1-benzoate[5] (2 g.) in 5% hydrochloric acid (30 g.), with cooling at 0~2° and occasional test with potassium iodide-starch paper. The precipitated diazo-oxide was collected, and washed with water. Pale yellow crystals melting at 117~119° with decomposition (yield nearly theoretical). Found: N, 11.75. Calculated for C_{13}-

(1) R. Willstätter and M. Benz, *Ber.*, **39**, 3495 (1906).

(2) *Ber.*, **20**, 1121, 1145 (1887).

(3) *Ber.*, **44**, 2387 (1911).

(4) For molecular structure and estrogenic activity see: M. Oki and Y. Urushibara, This Bulletin, **25**, 109 (1952).

(5) D. H. R. Barton, W. H. Linnell and N. Senior, *J. Chem. Soc.*, **1945**, 433.

$H_8O_8N_2$: N, 11.66%.

The diazo-oxide (1.8 g.) was added gradually with stirring to a solution prepared from potassium carbonate (5 g.), resorcinol (2 g.), and water (100 cc.). After standing overnight the reaction mixture was acidified with dilute hydrochloric acid, and the precipitate was collected and recrystallized from methanol (yield 2 g.). 2, 4, 2', 4'-Tetrahydroxyazobenzene 4-benzoate thus obtained forms yellow crystals melting at 235°. Found: N, 7.95. Calculated for $C_{19}H_{14}O_5N_2$: N, 8.00%.

The above benzoate (1.5 g.) was dissolved in 15 % aqueous caustic potash, and the solution was heated for a few minutes on a waterbath, left to stand overnight, and acidified with hydrochloric acid. Repeated recrystallization of the precipitate from methanol with use of active charcoal gave 2, 4, 2', 4'-tetrahydroxyazobenzene in fine orange-colored crystals (yield 1 g.). It did not melt but turned black gradually at 265~300°. Found: N, 11.10. Calculated for $C_{12}H_{10}O_4N_2$: N, 11.38%.

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